Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Journal of
Materials Chemistry A

Materials for energy and sustainability
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ARTICLE

Interface engineering of perovskite solar cells with PEO for improved performance

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Interface engineering was an important and efficient way to further improve the conversion efficiency of perovskite solar cells. In this study, we reported using a thin layer of PEO to modify the electron transport layer (ETL). Characterizations showed that PEO was uniformly coated on top of the original TiO_x ETL, without resulting in obvious change of the surface morphology, hydrophilic ability and transparency. With the interface dipole formed at the interface, the work function of the ETL decreased largely. Compared with devices with TiO_x only, devices based on the modified ETL gave a nearly 15% enhancement on the overall conversion efficiency, with both V_{oc} and J_{sc} improved. Further study showed that the improved performance should mainly be attributed to the better retarded back recombination and enhanced electron collection efficiency by means of the PEO thin layer modification.

1. Introduction

Organic-inorganic hybrid perovskite solar cell has been a quite hot research topic recently due to its fast improved power conversion efficiency (PCE).[1-4] The latest record certified by National Renewable Energy Laboratory (NREL) was 20.1%, which was very close to its theoretical PCE. With the increase of the PCE, the structures of this kind of solar cells have also developed. At the beginning, classical structure of dye-sensitized solar cells was adopted, with mesoporous TiO_2 as the electron collection and transport layer.[5,6] Then devices with insulating nanoparticles (such as Al_2O_3, ZrO_2) as scaffolds have also been reported and got great success.[7,8] Planar structured perovskite solar cells were also widely researched and gave quite good results.[9,10]

For most of the structures, a thin layer of TiO_2 or ZnO was commonly used on transparent conductive electrode (usually FTO or ITO) as the electron transport layer (ETL). With matched energy level, it could prevent holes formed in the perovskite or hole transport layer (HTL) from reaching the conductive electrode, which would lead to back recombination and reduced short-circuit current. To further improve the performance of the solar cells, optimization for this layer was an effective way. Snaith et al. developed a low temperature route for creating TiO_2 compact layer with decreased series resistance and hence resulted in improved fill factor and efficiency.[11] Yang Yang group doped the TiO_2 with Yttrium to enhance this layer's electron extraction and transport ability. The highest efficiency of 19.3% in a planar geometry was

finally got.[9] Except the doping strategy, to modify this layer with other materials was also a good choice to improve the device's overall performance.[12] This was a usual method adopted by researchers for organic solar cells and polymer solar cells. Self-assembled functional molecular layer or a thin layer of polymer (such as polyoxyethylene, polyethylenimine) for modification was reported.[13-17] The work function of the ETL could be tuned and the back recombination could be retarded due to the presence of interfacial dipole; the series resistance could also be reduced with modification. All these should contribute to an improved performance.

Here, we reported using a thin layer of polyoxyethylene (PEO) to modify the TiO_x blocking layer for perovskite solar cells with Al_2O_3 mesoporous films as scaffolds. As a kind of widely used polymer, PEO had various advantages making it an ideal material for the interface engineering of ETL, such as cheap, environment friendly, high transmittance, high polarity and easy to form uniform film. Ultraviolet photoelectron spectroscopy (UPS) result showed that with the PEO modification thin layer, work function of the ETL decreased largely. Devices with PEO modified TiO_x as ETL had improved V_{oc} and J_{sc}, and gave a nearly 15% enhanced overall power conversion efficiency (PCE) compared with control devices with bare TiO_x as ETL. Further characterizations showed that the electron-hole recombination was significantly retarded with the PEO modification, leading to higher electron collection efficiency and finally improved performance.

2. Experimental Section

2.1 Materials and Reagents.

All solvents and reagents were used as received. $PbCl_2$ (99.999%), Al_2O_3 nanoparticles dispersion in isopropanol (<50nm, 20 wt%), Poly (ethylene oxide) (average Mv 2,000,000) were all purchased from Sigma Aldrich. Super dehydrated solvents of dimethyl formamide, toluene and acetonitrile were purchased from J&K. CH_3NH_3I (MAI) was purchased from Xi'an Polymer Light Technology Cor., China.

2.2 Devices Fabrication.

TiO_x ETL was fabricated on FTO glass through atomic layer deposition (ALD) method. The perovskite solar cells were fabricated with a similar process of Snaith's group with optimized parameters: a thin layer of Al_2O_3 scaffold was spin-coated on the substrate at a rotation speed of 6000rpm for 60s, then drying at 150^OC hotplate for 30min. Perovskite layer was prepared by spin-coating from homogeneous 40 wt% precursor solution ($PbCl_2$:MAI =1:3, in DMF) and annealed at 100^OC for 90min. After cooled down to room temperature, the HTL layer was spin-coated on top with a spinning speed of 2500rpm, for 60s. Finally, 50 nm thick gold electrode was deposited by thermal evaporation through a shadow mask. The active area of studied devices was 10 mm^2. For the devices with PEO modification, a solution of PEO/acetonitrile was spin-coated on the ALD-TiO_x layer at 5000rpm for 60s and then dried at 60^OC for 15min to move the residual solvent.

2.3 Characterizations.

The current-voltage curves (J-V cureves) and electrochemical impedance spectroscopy (EIS) were measured by ZAHNER CIMPS electrochemical workstation (Germany) under solar simulator (Xenon lamp, Oriel, AM 1.5). The incident light intensity was calibrated with a standard crystalline silicon solar cell. The total active area of the device was 10mm^2. The IPCE spectra were measured in air with equipment developed by institute of physics, Chinese academy of sciences. The UV-vis absorption spectra were tested with the Hitachi Model U-3010 UV-vis spectrophotometer. XPS spectra were tested with the PHI 5300ESCA instrument and the spectra were calibrated with the C1s peak (284.8eV). PL decay spectra were recorded by a high resolution streak camera system (Hamamatsu C10910). All the samples were excited by 517nm at room temperature with 135 nJ cm^{-2}/pulse. Steady-state PL spectra were tested with a fluorospectrophotometer (Jobin Yvon, FluroMax-3). AFM images were carried out with SPA-400, Seiko.

3. Results and discussion

3.1 Physical characterizations for the films

AFM was carried out to characterize the surface morphology of the ETL without and with PEO thin layer. As shown in Fig.1,
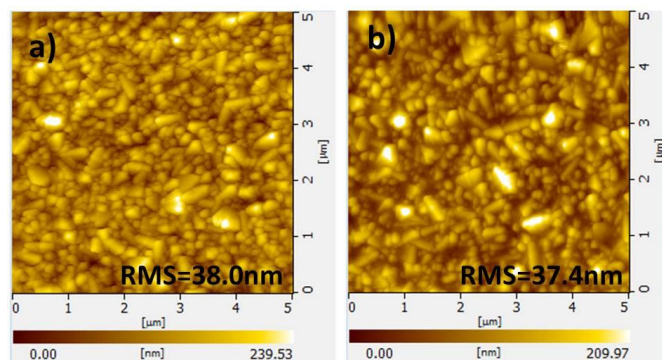

Fig.1 Atomic force microscopy images of (a) FTO/TiO_x and (b) FTO/TiO_x/PEO.

no clear morphology change was noticed. The surface root-mean-square (RMS) roughness decreased a little after spinning a thin layer of PEO. The result was as we expected because both the ALD TiO_x and PEO should form a uniform coating on the surface of FTO. Fig. S1 showed the contact angle test for the surfaces. Both the films showed a quite good hydrophilic ability. This was quite important for the high conversion efficiency perovskite solar cells because it made sure that the perovskite precursor solution could infiltrate into the mesoporous Al_2O_3 scaffolding and form a good and compact contact with the ETL. We tested the dissolving ability of PEO in isopropanol (IPA, solvent for Al_2O_3 nanoparticles) and dimethyl formamide (DMF, solvent for perovskite precursor) to indirectly check the solvent resistance of the PEO layer and the results were shown in Fig. S2. PEO with high molecular weight had a quite bad solubility in IPA and DMF. As a result, the PEO layer shouldn't be largely changed by the followed process. The cross section image of device with PEO was shown in Fig S3.No clear PEO layer was noticed, indicating this layer was thin.
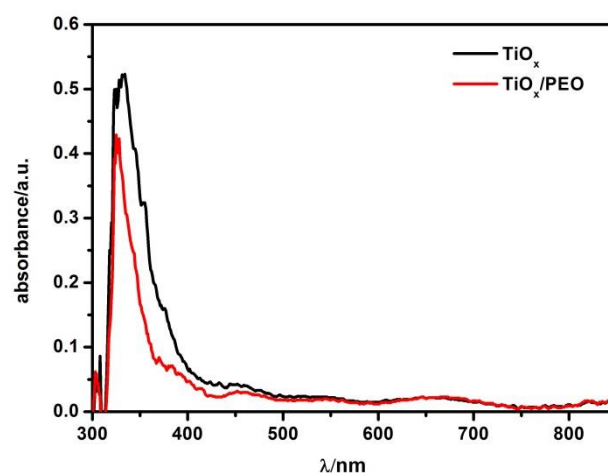

Fig.2 UV-vis absorption curves of TiO_x and TiO_x/PEO spun on FTO glass as hole blocking layer.

Fig.2 showed the UV-vis absorption spectra of the TiO_x and TiO_x/PEO films deposited on FTO glass. In the wavelength longer than 400nm, both the films showed little absorption,

allowing most of the incident light to reach the active layer. The absorption onset of the TiO_x/PEO film exhibited a blue shift compared with the bare TiO_x film, which might be due to the change in scattering cross section of TiO_x/PEO layer.
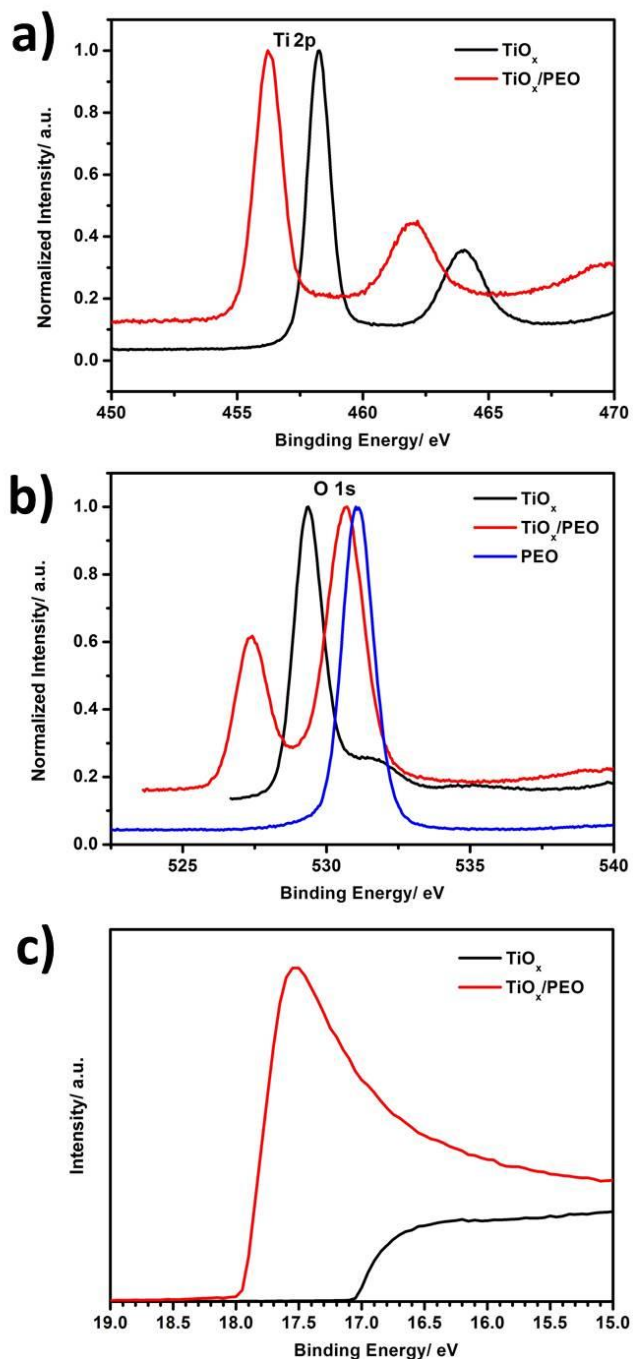

Fig.3 XPS focus on the (a) Ti2p and (b) O1s peaks for FTO/TiO_x and FTO/TiO_x/PEO films. (c) UPS spectra of TiO_x and TiO_x/ PEO films. The light source of UPS was a He1 discharge lamp ($hv = 21.2eV$).

The X-ray photoelectron spectroscopy (XPS) of the TiO_x and TiO_x/PEO were shown in Fig. 3 (a) and (b) and the survey of the XPS spectra was shown in Fig. S4. To check the position of O1s peak from PEO, a thick PEO film deposited on FTO with

10mg/ml concentration at 5000rpm was used. We could notice that, with a thin layer of PEO on top, Ti2p and O1s peaks belonging to TiO_x films were shifted to a lower binding energy, indicating the electronic interaction between the TiO_x and PEO. The similar shift of peaks was also found for the PEI modified TiO_x films.[15] The Ti2p peak was clearly observed from the TiOx/PEO film. This indicated that the PEO layer was quite thin, which should only be several nanometers. Ultraviolet photoelectron spectroscopy (UPS) was further carried out to measure the energy level change of the ETL. Results (Fig. 3(c)) showed that the work function of ETL dropped from 4.15 to 3.25 eV with a thin layer of PEO spun on. This work function change should be contributed to the dipole layer formed by the PEO. Similar phenomena had been extensively observed by others.[16,18] The decrease of the work function of the ETL could increase the built-in potential inside the devices, which could not only lead to the increased V_{oc} but also enhance the extraction of the charge carriers from the absorption layer, and therefor increased J_{sc}.[15]

3.2 Photovoltaic performances

Table 1. Performance summary of the perovskite solar cells with different thickness of PEO films as surface modification layer.

	Voc [V]	Jsc [mA/cm²]	FF	PCE [%]
Control	1.00	17.9	0.66	11.8
1mg/mL	1.01	18.6	0.67	12.5
2.5mg/mL	1.02	20.7	0.65	13.8
5mg/mL	1.01	18.7	0.60	11.4
Control (average±s.d.)[a]	1.03±0.03	17.1±1.1	0.61±0.03	10.8±0.90
2.5mg/mL (average±s.d.)[a]	1.05±0.03	19.0±0.8	0.62±0.02	12.3±0.64

[a]The average and standard deivation (s.d.) of the 18 cells from 3 different batches processed at the same conditions.
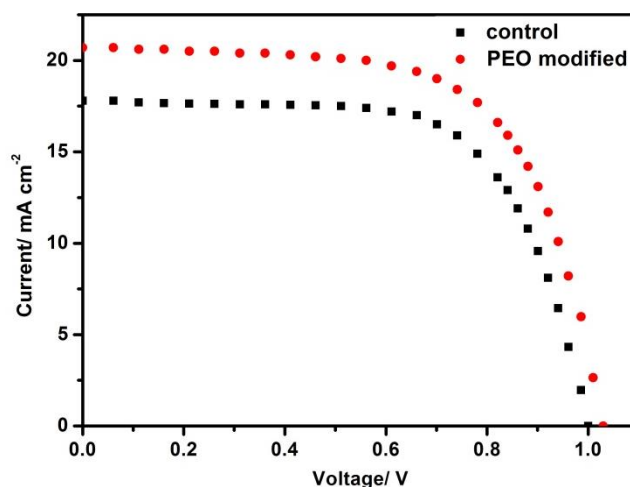

Fig.4 *J-V* characteristics of solar cells based on TiO_x and optimized TiO_x/PEO ETL under one sun irradiance (100 mW/cm² photon fulx).

The current-voltage *(J-V)* characteristics of the devices based on ETL without and with PEO were shown in Table 1 and Fig. 4. The results were got in the reverse scanning direction with a 50mV/s scanning speed, from 1.1 V to 0V. To optimize the thickness of the PEO film, solutions with different concentrations were used for the spinning coating. The control device with bare TiO_x showed an open-circuit voltage (V_{oc}), short-circuit photocurrent density (J_{sc}), fill factor (FF) of 1.00V, 17.9 mA/cm^2 and 0.66, respectively, leading to a PCE of 11.8%. With a thin layer of PEO, both the V_{oc} and J_{sc} of the solar cells increased. For the optimized thickness (from 2.5 mg/mL solution), a PCE of 13.8% was got, enhanced more than 15% compared with control device. Further increasing the thickness of PEO gave a reduced PCE. We thought that was due to the decreased electron transport ability of the ETL. Distribution of the photovoltaic parameters got from 18 devices was shown in Fig. S5. *J-V* curves tested under different scanning direction were shown in Fig. S6. For both devices with TiO_x and TiO_x/PEO used as ETL, the hysteretic behaviour was observed. Though this was a common problem for perovskite solar cells, the reasons for it were still under research.[1,19,20]
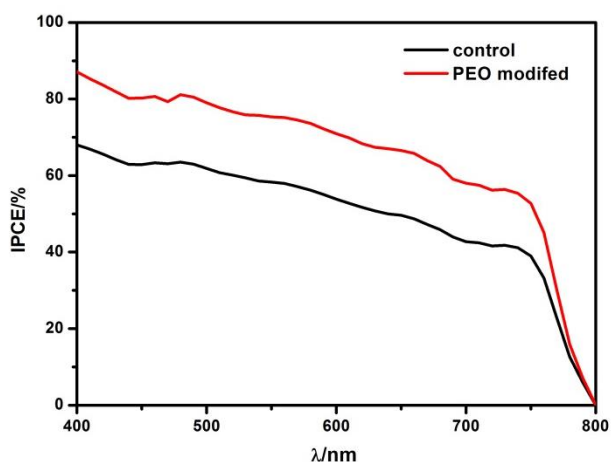

Fig.5 IPCE spectrum of solar cells based on TiO_x and optimized TiO_x/PEO ETL.

The incident photo-to-electron conversion efficiency (IPCE) spectrum of the control device and optimized device were presented in Fig.5. In the range of 400-750nm, device with PEO modified ETL gave an enhanced IPCE, what was consistent with the improved J_{sc}.

3.3 Discussion about the improved IPCE and performance.

We tried to better understand the improved IPCE, which could be given by the following equation:

$$IPCE(\lambda)=LHE(\lambda)\varphi_{inj}\eta_{col}$$

where LHE was the light-harvesting efficiency by the active layer, φ_{inj} was the electron injection efficiency from the perovskite layer to the electron collection layer, and η_{col} was the charge collection efficiency at the electrodes.[21]
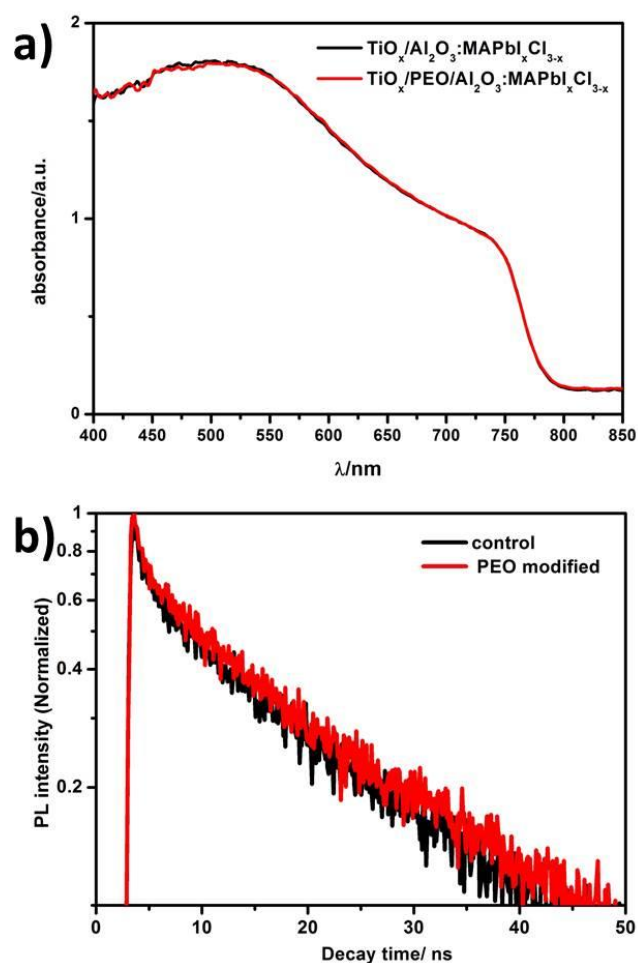

Fig.6 (a) UV-vis absorption of the perovskite active layers for solar cells; (b) PL decay spectra of films: $FTO/TiO_x/MAPbI_xCl_{3-x}$ (black curve) and $FTO/TiO_x/PEO/MAPbI_xCl_{3-x}$ (red curve).

We firstly measured the absorption spectrum of the perovskite films to check the active layers' LHE. As shown in Fig. 6(a), no difference was found for the films without or with PEO layer. This was not hard to understand. As mentioned before, both the morphology and the surfaces' hydrophilicity hadn't changed a lot after spinning a layer of PEO, so the active layer should not be affected by the inserted PEO layer. The φ_{inj} was positively related to the ETL's electron extraction ability from the perovskite layer, what could be measured with the photoluminescence spectroscopy (PL) decay.[22] As shown in Fig. 6(b), with a thin layer of PEO, the PL quenching was slightly reduced, indicating it was a little hard for the electrons to inject into the hole-blocking layer. That meant the PEO reduced the φ_{inj} mildly due to its insulating property. This was also confirmed by the enhanced steady state PL for the TiO_x/PEO/perovskite sample, as shown in Fig. S7. Now that the LHE had remained constant and the φ_{inj} even a little decreased, the enhancement of IPCE should be contributed to the improved η_{col}.
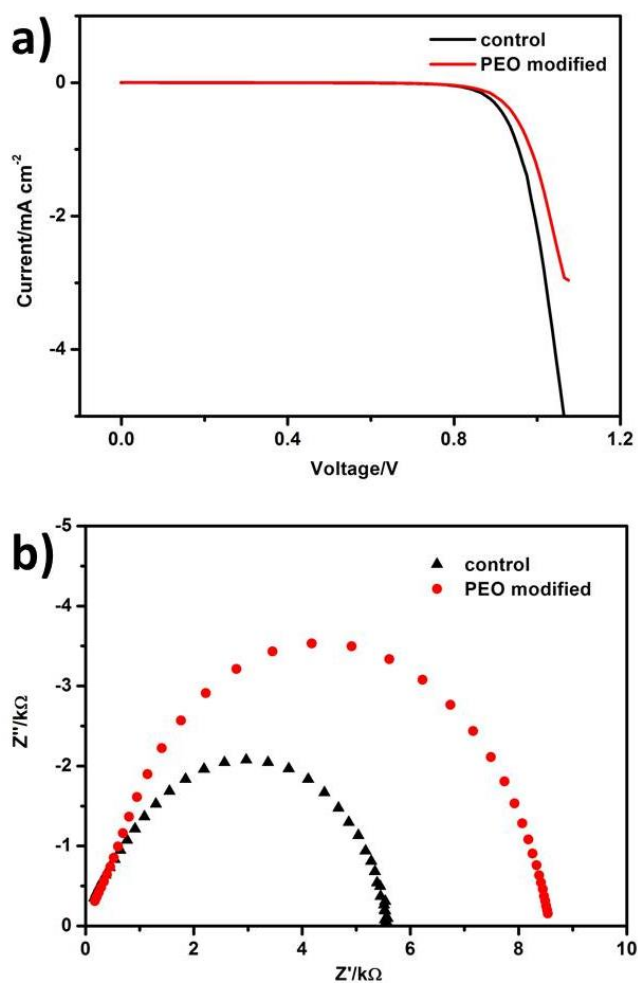
Fig.7 (a) *J-V* characteristics of solar cells based on TiO_x and optimized TiO_x/PEO ETL tested under dark; (b) EIS spectra of solar cells based on TiO_x and optimized TiO_x/PEO ETL tested under dark with a 0.9V bias voltage.

The charge collection efficiency (η_{col}) cumulatively took into account the transport and recombination dynamics and could be defined by the following equation[23]:

$$\eta_{col}= \text{transport rate}/ (\text{transport rate} + \text{recombination rate})$$

We measure the *J-V* curves and EIS spectra to check the charge collection situations inside the devices. Fig. 7(a) showed the *J-V* curves of devices measured in dark. Onset of the dark current of device based on TiO_x/PEO ETL shifted to a higher voltage with respect to device based on TiO_x ETL. As reported, the shift in the onset of the dark current and the corresponding increase in the V_{oc} should have resulted from the recued back recombination happened at the interfaces, mainly the back flow of electrons from the blocking layer to the perovskite layer or hole transport layer.[24,25] Electrochemical impedance spectroscopy (EIS) was carried out to further characterize the blocking effect of the PEO layer inside the solar cells. Fig. 7(b) showed the EIS spectra measured under dark at an applied potential of 0.9V, from 10^5 to 0.1 Hz. Most part of the spectra corresponded to the lower frequency. As reported, spectra in

the low-frequency range were related to interfacial recombination between electrons and holes, which had a positive correlation with recombination resistance of the solar cells (R_{rec}).[26,27] It could be clearly found that R_{rec} increased largely for the TiO_x/PEO blocking layer. As had found in the dye-sensitized solar cells, the increase of R_{rec} would reduce the recombination kinetics by about 2 orders of magnitude, so the charge recombination at the interface would be significantly retarded, consistent with the conclusion from the dark J-V curves. Anyway, both the dark current and EIS results indicated that inside the devices, the back recombination was retarded with a thin layer of PEO, leading to a higher η_{col}.

Thus, out of the three parameters defining the IPCE, LHE had remained constant and φ_{inj} decreased a little upon addition of the PEO modification overlayer on the TiO_x blocking layer. In contrast, the appreciable gain in charge collection efficiency offset the loss in injection efficiency and served to explain the enhanced IPCE and J_{sc} observed for devices with the PEO modification layer.

4. Conclusions

In summary, we introduced PEO thin layer into perovskite solar cells for surface engineering of the electron transport layer. It was uniformly coated on top of the TiO_x, without changing the ETL's morphology, transparency and hydrophilicity. Due to the dipole formed at the interface, work function of the ETL decreased with a thin layer of PEO. Compared with devices with TiO_x only, devices based on the modified ETL gave a nearly 15% enhancement on the overall conversion efficiency, with both V_{oc} and J_{sc} improved, what should mainly be attributed to the better retarded back recombination and enhanced electron collection efficiency by means of the PEO thin modification layer. The results implied that interface engineering could be an effective approach to further improve the performance of the perovskite solar cells.

Notes and references

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† Electronic Supplementary Information (ESI) available: [contact angle test, cross section image, PEO dissolving situation in solvents, distribution of photovoltaic parameters, *J-V* curves tested with different scanning direction and steady-state PL results] See DOI: 10.1039/b000000x/

1. F. Service, *Sci.*, 2014, **344**, 458.

2. Y. Z. Ma, S. F. Wang, L. L. Zheng, Z. L. Lu, D. F. Zhang, Z. Q. Bian, C. H. Huang and L. X. Xiao, *Chin. J. Chem.*, 2014, **32**, 957-963.

3. P. Gao, M. Gratzel and M. K. Nazeeruddin, *Energy Environ. Sci.*, 2014, **7**, 2448-2463.

4. S. Q. Luo and W. A. Daoud, *J. Mater. Chem. A*, DOI: 10.1039/c4ta04953e

5. A. Kojima, K. Teshima, Y. Shirai and T. Miyasaka, *J. Am. Chem. Soc.*, 2009, **131**, 6050-6051.

6. 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.

7. M. M. Lee, J. Teuscher, T. Miyasaka, T.N. Murakami and H. J. Snaith, *Sci.*, 2012, **338**, 643-647.

8. D. Bi, S.-J. Moon, L. Haggman, G. Boschloo, L. Yang, E. M. J. Johansson, M. K. Nazeeruddin, M. Gratzel and A. Hagfeldt, *RSC Adv.*, 2013, **3**, 18762-18766.

9. H. P. Zhou, Q. Chen, G. Li, S. Luo, T. Song, H. Duan, Z. R. Hong, J. B. You, Y. S. Liu and Y. Yang, *Sci.*, 2014, **345**, 542-546.

10. D. Liu and T. L. Kelly, *Nat. Photon.*, 2014, **8**, 133-138.

11. J. M. Ball, M. M. Lee, A. Hey and H. J. Snaith, *Energy Environ. Sci.*, 2013, **6**, 1739-1743.

12. Q. Hu, J. Wu, C. Jiang, T. H. Liu, X. L. Que, R. Zhu and Q. H. Gong, *ACS Nano*, 2014, **8**, 10161-10167.

13. H.-L. Yip, S. K. Hau, N. S. Baek, H. Ma and A. K.-Y. Jen, *Adv. Mater.*, 2008, **20**, 2376-2382.

14. A. Y. Li, R. M. Nie, X. Y. Deng, H. X. Wei, S. Z. Zheng, Y. Q. Li, J. X. Tang and K.-Y. Wong, *Appl. Phys. Lett.*, 2014, **104**, 123303.

15. D. Yang, P. Fu, F. J. Zhang, N. Wang, J. Zhang and C. Li, *J. Mater. Chem. A*, 2014, **2**, 17281-17285.

16. Y. H. Zhou, F. H. Li, S. Barrau, W. J. Tian, O. Inganas and F. L. Zhang, Sol. *Energy Mater.Sol. Cells*, 2009, **93**, 497-500.

17. C. He, C. M. Zhong, H. B. Wu, R. Q. Yang, W. Yang, F. Huang, G. C. Bazan and Y. Cao, *J. Mater. Chem.*, 2010, **20**, 2617-2622.

18. Y. Zhou, L. Y. Yang, W. J. Qin and S. G. Yin, *J. Renewable Sustainable Energy*, 2014, **6**, 043108.

19. T. Salim, S. Sun, Y. Abe, A. Krishna, A. C. Grimsdale and Y. M. Lam, *J. Mater. Chem. A*, 2015, DOI: 10.1039/C4TA05226A.

20. H.-S. Kim and N.-G. Park, *J. Phys. Chem. Lett.*, 2014, **5**, 2927-2934.

21. M. Grätzel, *Acc. Chem. Res.*, 2009, **42**, 1788-1798.

22. A. K. Chandiran, M. K. Nazeeruddin and M. Gratzel, *Adv. Funct, Mater.*, 2014, **24**, 1615-1623.

23. A. K. Chandiran, N. Tetreault, R. Humphry-Baker, F. Kessler, E. Baranoff, C. Yi, M. K. Nazeeruddin and M. Gratzel, *Nano Lett.*, 2012, **12**, 3941-3947.

24. A. K. Chandiran, A. Yella, M. T. Mayer, P. Gao, M. K. Nazeeruddin and M. Gratzel, *Adv. Mater.*, 2014, **26**, 4309-4312.

25. Y. X. Zhao and K. Zhu, *J. Phys. Chem. Lett.*, 2013, **4**, 2880-2884.

26. X. B. Xu, H. Zhang, K. Cao, J. Cui, J. F. Lu, X. W. Zeng, Y. Shen and M. K. Wang, *ChemSusChem*, 2014, **7**, 3088-3094.

27. J. Dong, Y. Zhao, J. Shi, H. Wei, J. Xiao, X. Xu, J. Luo, J. Xu. D. Li, Y. Luo and Q. Meng, *Chem. Commun*., 2014, 50, 13381-13384.

Table of contents entry

A thin PEO layer was spin-coated on top of TiO_x to modify the ETL for improved electron collection efficiency and better retarded back recombination, and therefore enhanced device performance.