W-doped TiO$_2$ as electron transport layer for high performance solution-processed perovskite solar cells

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Abstract

In this work, W‑doped TiO_2, was successfully fabricated, as electron transport layer (ETL) in perovskite solar cells (PSCs) *via* low-temperature solution-processed method, whose outstanding performances were verified. The experimental results reveal that, W^{6+} was doped into the TiO_2 lattice successfully. The improved ETL exhibit significantly improved on conductivity, transport and extraction of photo-generated carriers and less trap-state density as compared with the pristine TiO_2 films. Meanwhile, strengthening the velocity of carrier and collection of sufficient charge can efficiently increase short-circuit current (J_{SC}) which favor an improved fill factor (FF) and a higher power conversion efficiency (PCE). Our optimized cation-anion-mixed PSC based on W-doped TiO_2 has achieved an efficiency of 18.85%. This improved PCE is almost 28.1% higher than that of the pure TiO_2. This study provides a promising approach to design metal-doped TiO_2 for fabricating high-performance perovskite solar cells.

1. Introduction

Organic−inorganic hybrid halide perovskite solar cells (PSCs) have been considered as a promising photovoltaic device which may replace the traditional silicon solar cells for solar energy harvesting since its adjustable bandgap, low rate of recombination, redundant electron-hole diffusion length and simple fabrication procedure[1-3]. TiO_2 are generally employed as the electronic transporting layer (ETL) in the N-I-P structure of PSCs. From 2009 to now, a rapidly rise of power conversion efficiency (PCE) for PSCs (from 3.8% to 25.2%) has been witnessed[4-7]. In PSCs, transporting electrons, blocking holes and avoiding them recombination are the major functions of the ETL [8-10]. Metal oxides like TiO_2, ZnO, SnO_2, WO_x and WO_x-TiO_x *etc.*, were frequently used in previously reported literatures[11-16]. In Hao's team, several optimized ETL were employed in getting the high-efficiency and stable performance PSCs, for instance, polyelectrolyte-doped SnO_2[17], coupled-ZnO layer[18], heterojunction-contact NiO[19]. Among the commonly used ETL in PSCs, TiO_2 has demonstrated superiorities such as excellent electron conductivity, well matching with the energy band of perovskite layer and ease in fabrication[20-25]. Therefore, it is quite essential to fabricate excellent TiO_2 layer for high-efficiency PSCs. However, TiO_2 has to be sintered at a high-temperature (> 450 °C) to obtain crystallinity and high carrier mobility[26], which complicates the preparation technology and confines the development of the flexible device. To address these issues, several novel low-temperature (<150 °C) deposition methods have been developed to fabricate TiO_2 ETL

such as chemical bath deposition (CBD)[27, 28], atomic layer deposition[29-31] and magnetron sputtering[32, 33]. Among them, Aswani Yella *et al.* have successful fabricated the rutile TiO_2 through low-temperature (<100 °C) solution process[34]. In Ma's report, NaCl was doped on TiO_2 to passivate the interface of ETL and perovskite through solution-processed method at 70 °C[35]. MXene and bis-PCBM have been utilized to optimize the PSCs' device efficiency and stability by Ye *et al.* by solution process[36, 37]. Recently, a two-fluid spray coating method has been developed by Wu *et al.* to synthesize nanostructured TiO_2 under 150 °C[38].

TiO_2, on the other hand, is widely known as the n-type semiconductor which can be conducted by the oxygen vacancies formed in the preparation process. Nonetheless, owing to the lower migration rate of carriers and deep level defects in TiO_2, electrons formed in the perovskite layer can not transport efficiently and the proposed devices always suffer with a low performance. Doping mental ions is a valid way to boost the carrier concentration of semiconductors and reduce deep level defects[39]. To date, metal ions such as lithium[40, 41], magnesium[42-44], zinc[45], aluminum[46] and rubidium[47] have been reported to be doped into the TiO_2 lattice accordingly[48]. Niobium-doped TiO_2 as the ETL will increase the conductive path and strengthen the contact of interface in PSCs[49]. Yttrium-doped TiO_2 and Tin-doped TiO_2 have been used in PSCs to enhance electron extraction and transport and suppress the carrier recombination in interface[50, 51]. Tungsten-doped TiO_2 was utilized as photoanode

in PSCs and produced a PCE of 10.6%[52]. Even if these strategies can ameliorate the defects as mentioned above, their preparation methods are all suffered from a high annealing temperature (300-500 °C), which largely limited the manufacture of large-area devices and the applications on flexible substrates. Therefore, seeking one solution method to prepare optimized TiO_2 at low temperature is imperative and certainly a worthwhile subject.

In this work, one low-temperature solution method to obtain the crystallized TiO_2 film doped by W^{6+} was designed, which can extract more carriers on the interface between ETL and perovskites. According to the previous report, tungsten has been widely used in optimization on the performance for PSCs[52-59]. Among them, W-doped TiO_2 ETL and WO_x/TiO_2 bilayer have presented smoothy ETL with high crystallinity and enhanced conductivity. Although these demonstrated enhancements in TiO_2 optimized by W make this effective ETL for efficient PSCs, such as boost the carrier concentration and passivate the trap states in TiO_2, most of them are suffered from the high-temperature fabrication process. As shown in **Fig. 1**, in contrast with these previous studies, the solar cells in this work have shown excellent performance, given the short circuit current (J_{sc}), power conversion efficiency (PCE) and fabrication temperature[15, 41, 52-58]. In addition, optimized PSC with an 0.3 mol% W-doped TiO_2 as ETL and the mixed perovskite material based on $Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.83}Br_{0.17})_3$[60] as light absorption layer has achieved a better performance, including the J_{sc} increasing

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from 22.73 mA/cm^2 to 24.26 mA/cm^2 and the fill factor (FF) from 58.37% to 69.22%.

As a consequence, a substantially PCE of 18.85% has been achieved.

2. Experimental section

2.1 Materials

Tungsten chloride (WCl_6, 99.9% metals basis) was purchased from Sigma Aldrich. Dimethysulfoxide (DMSO), γ-butyrplactone (GBL) and chlorobenzene were bought from Alfar Aesar. PbI_2, Li-TFSI, Spiro-OMeTAD, 4-tert-butyl pyridine and methylamminium iodide (MAI) were bought from Xi'an Polymer Light Technology Corporation.

2.2. Fabrication of perovskite solar cells

The fabrication process of PSCs starts with commercially available F-doped SnO_2 (FTO) substrates with a sheet resistance of 8 Ω^{-2} and more than 82% optical transmission in the visible light range, which were pre-cleaned. With deionized water, acetone and isopropyl alcohol, the cleaned substrates were treated in the UV-ozone for 15 min so as to improve the formation of TiO_2 layer. To prepare the precursor solution, the $TiCl_4$ solution was diluted into deionized water to 200 mM at 0 °C. WCl_6 was dissolved into ethyl alcohol to prepare solution with different mole ratios (0.1%, 0.3%, 0.5%), then they were dropped into the diluted $TiCl_4$ solution, respectively, to form the precursor solution. Next, the cleaned FTO substrates were immersed to the precursor solution at 70 °C for 1 h. Finally, the substrates deposited with TiO_2 were

cleaned with deionized water and ethanol and then dried at 120 °C for 1h.

To prepare the perovskite active layer, FAI, PbI_2, MABr and $PbBr_2$ (1:1.1:0.2:0.22 M ratio) were stirred in a mixture of DMF: DMSO: N-methyl-2-pyrrolidone (NMP) (the volume ratio is 16:4:1) in a dry gas environment. CsI was added in the DMSO solution (the volume ratio is 5:95), then it was put into the first mixed solution at 60 °C for around 2 h. Then, the mixed perovskite precursor solution was spin-coated on TiO_2 layer by a two-step process involving a low-speed spinning at 1000 rpm for 10 s and a high-speed spinning at 6500 rpm for 20 s, respectively. Chlorobenzene antisolvent was dropped on substrates at the 25th second. Next, substrates were annealed at 100 °C for 1 h. The sprio-OMeTAD layer was spin-coated on top of the perovskite film as the hole transport layer at 3000 rpm for around 30 s. Gold electrode (80 nm) was eventually deposited through the Trovato thermal evaporation at 7×10^{-6} Torr, and the area of this device is 0.04 cm^2.

2.3. Instruments

X-ray diffraction (XRD) patterns were analyzed by Rigaku Ultima IV with a 0.1541 nm Cu Ka line. Thermo Scientific Escalab 250Xi was used to obtained the X-ray photoelectron spectroscopy (XPS) and Ultraviolet photoelectron spectroscopy (UPS) information. V-730 Jasco spectrometer was employed to obtain the absorption spectra. The morphology of the sample was measured by the scanning electron

microscopy (SEM) and atomic force microscopy (AFM) with SU-8010 HITACHI and

Quanta 200 FEG, FEI. The current density-voltage (J-V) measurements were got by

300 W xenon lamp (Newport 66984). Keithley 2400 system and $100\,mW/cm^2$ AM

1.5 G standard Newport sun simulator. Incident photo-to-current conversion

efficiencies (IPCE) was employed by Zolix, Solar Cell Scan100. Steady-state

photoluminescence (PL) and time-resolved photoluminescence (TRPL) data were

analyzed by FLS1000 spectrometer. Electrochemical impedance spectroscopy (EIS)

was tested by a Donghua DH7000 electrochemical workstation. Film surface roughness

were

3. Results and discussion

Firstly, we placed the FTO substrates into the prepared precursor solution. After

cleaning and drying, the W-doped TiO_2 with different concentrations was coated on the

FTO substrates. As shown in **Fig. 2a**, XRD was utilized to analyze the crystallinity of

prepared W-doped TiO_2 films and confirm that TiO_2 is characterized by the rutile

phase[61]. From tetragonal structure of TiO_2 [JCPDS Card No. 21-1276], diffraction

peaks at 25.3°, 37.7°, 48.0°, 53.9°, 62.8° and 68.8° can be ascribed to the (101), (004),

(200), (105), (213) and (116) crystal planes[61]. Apparently, all peaks shown are

similar no matter how many dopants are doped in TiO_2 and characteristic peaks of WO_3

are not appeared. Further more, the crystallinity of TiO_2 did not transform after doped

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with tungsten. Since the W^{6+} has the similar ionic radius with Ti^{4+}, the W^{3+} was hence doped into the lattice of TiO_2 by the lattice replacement, which is well consistent with the previous studies on W-doped TiO_2[62, 63]. Besides, there is no obvious peak shift and change of full width in half-maximum of rutile phase diffraction (101), which means that the different doping contents do not change the rutile crystal and crystallinity heavily (**Fig. 2b**). **Fig. 2c and d** show the SEM images of the pristine and 0.3 mol% W-doped TiO_2. In Fig. S1, atomic force microscopy (AFM) was carried out to characterize the surface morphology. The root mean square (RMS) roughness of W-doped TiO_2 (RMS:17.8 nm) exhibits less hole than pristine TiO_2 (RMS:13.7 nm). A more compact TiO_2 layer is formed after W doping, which suggests that the W doping contributes to the formation of a dense and smooth morphology with a lower recombination site, and an efficient carrier transport ability can be expected accordingly.

XPS was used to analyze the chemical element of W in TiO_2. **Fig. 3a** shows the electron binding energy of O 1s, Ti 2p and 0.3 mol% W-doped TiO_2 sample and proves that the existence of W element in 0.3 mol% W-TiO_2. In **Fig. 3b and c,** detail information of Ti 2p and O 1s spectra are then exhibited. Binding energy peaks at 458.6 and 458.7 eV are corresponding to $Ti^{4+}2p$ 3/2 of pure and doped TiO_2, respectively. The Ti 2p peak clearly shows a slight up-shift after optimization since the different electronegativity among titanium atoms (1.54) and tungsten atoms (2.36), indicating negative charge transfer to tungsten in Ti-O-W bond[64]. Hence, the core level binding energy of Ti 2p

will be increased. Moreover, considering the similar radius of W^{6+} (0.605 Å) and Ti^{4+} (0.60 Å), W^{6+} ions can displace Ti^{4+} easily, forecasting that W is involved in the lattice of TiO_2[63, 65]. The peaks at 531.26, 529.8 eV for undoped TiO_2 and 531.39, 529.75 eV for 0.3 mol% W-doped TiO_2, respectively. After deconvolution of O 1s in Fig. S2b, 0.3 mol% W-doped TiO_2 shows four peaks. The peaks at 532.07 and 531.27 eV are assigned to O_2 molecules and -OH assembled on surface, where the peaks at 530.14 and 529.55 eV are correspond to oxygen vacancies and Ti-O-W bound after doping tungsten ions[66]. Some people alleged the peak at 530.14 eV is characteristic of the W-O bound[65, 67]; Nevertheless, others claimed it should be the -OH assembled on the surface[68]. Hence, the metal-oxygen increase is consistent with XPS analysis, and this slight higher chemical shift indicates W doping can influence the chemical states. The XPS result in **Fig. 3d** exhibits the W^{6+} 4f signals in pristine and 0.3 mol% W-doped TiO_2. Fig. S2c reveal two deconvoluted peaks of W $4f_{5/2}$ (37.6 eV) and W $4f_{7/2}$ (36.4 eV), indicating the W^{6+} appears in the W-doped TiO_2 layer[69]. Bind energy difference of two peaks is caused by Ti 3p level at 36.9 eV[70]. In other words, the presence of W is clearly shown in XPS and undetectable tungsten-associated phase found in XRD analysis which further indicates the W element is doped into the lattice of TiO_2 successfully.

To evaluate the function of W dopant on the direct-current conductivity (σ_0) of TiO_2 layer[71], we fabricated a device structured with FTO/TiO_2 layer/Au. The I–V curves

are displayed in **Fig. 4a** and σ_0 of various TiO$_2$ can be obtained using Eq. (1)

$$I = \sigma_0 AD^{-1}V \tag{1}$$

A represents the area of device (4 mm^2) and D represents for the TiO$_2$ thickness (70 nm). The σ_0 was calculated and shown in **Table S1**. It is clearly seen the σ_0 has increased with the increase of W doping ions. This result ascribed to the higher shift of Fermi energy for doping W element which will increase the amount of free electrons since forming additional oxygen vacancies on TiO$_2$. In **Fig. 4b**, to explore the carrier mobility of TiO$_2$ film, the current density voltage (J-V) curves of simple devices (FTO/pristine and 0.3 mol% W-doped TiO$_2$/PCBM/Ag) were obtained by Mott. Gurney Eq. (2)[72]

$$J = 9\varepsilon_0\varepsilon_r\mu_e V^2/8L^3 \tag{2}$$

J represents the current density, ε_r represents the dielectric permittivity of TiO$_2$, ε_0 is the vacuum permittivity, V stands for the device voltage, μ_e and L stand for electron mobility and thickness of the ETL. After calculation, the μ_e of pure TiO$_2$ and 0.3 mol% W-doped TiO$_2$ are 5.34×10^{-4} and 8.85×10^{-4}, respectively. It can manifest that W-doped method can enhance the electron mobility of TiO$_2$ film. The optical absorption spectra are generally used to show the energy gap and optical properties. A strong absorption appeared less 400 nm since the (O^{2-} to Ti^{4+}) ligand to metal charge transition[73] has shown in **Fig. 4c**. Blue shift of the absorption edge proves a large band gap formed, indicating it was enlarged after doping W element. E_g can be calculated directly through the Tauc plot in **Fig. 4d**. W-doped TiO$_2$ exhibits an increase from 3.03 to 3.1 eV,

compared with the undoped device. It reveals that the replacement of Ti^{4+} by W^{6+} results in a negative shift of conduction band minimum (CBM)[74]. UPS is employed to analyze the valence electron structure. It is clearly found the Fermi level (E_f) decrease from pristine TiO_2 (4.16 eV) to 0.3 mol% W-doped TiO_2 (4.12 eV) in **Fig. S3**. This up shift is due to high binding power of tungsten to oxygen which is even dislodged causing the vacancies formed when doping the W^{6+}, so the open-circuit voltage (V_{oc}) of PSC is improved and the conductivity of TiO_2 layer will be enhanced. The cross-section SEM image is demonstrated in **Fig. 5a**. After calculation, the energy-level diagram of the solar cell with the position of E_f, valence band maximum (VBM) and CBM is shown in **Fig. 5b** and the corresponding data are analyzed in **Table S2**. W-doped TiO_2 has a lower CBM than that of undoped TiO_2, assisting more direct injection electron generated from the perovskite into the TiO_2 conduction band. Hence, it will optimize electron accumulation and enhance transport between the TiO_2 and perovskite layer accordingly.

SEM images for top surface morphology of perovskite layer deposited on undoped TiO_2 and 0.3 mol% W-doped TiO_2 layer are shown in **Fig. 6a and b**. It is clearly seen that particles with porosity are aggregated on the ETL tightly and grain size becomes larger after doping W element. In **Fig. S4**, analyzed by software, distribution of the perovskite grain size is obtained from pristine and 0.3 mol% W-doped TiO_2, respectively. Obviously, perovskite layer coated on the doped TiO_2 has a larger mean grain size (750

nm), compared to that based on pure TiO_2 device (500 nm), which are beneficial for the PSCs. The crystallinity of perovskite films are characterized by XRD in **Fig. 6c**. As clearly seen, the peaks at 14.11°, 28.44° and 31.88° can be assigned to the diffractions from (110), (220) and (310) crystal planes for perovskite. These peaks show a vigorous intensity of diffraction, demonstrating a better crystallinity perovskite film via doping W into TiO_2. The strong intensity is most probably ascribed to the high crystallinity and large grain size of the perovskite layer. Meanwhile, this appearance also corresponds to the enhanced absorption in 0.3 mol% W-doped TiO_2 sample (**Fig. 6d**). The absorption spectrum are obtained through multilayer film FTO/pristine TiO_2/perovskite and FTO/0.3 mol% W-doped TiO_2/perovskite. After W-doping, the light-absorbing promotion is discovered, owing to band gap and transmittance of TiO_2 become larger and stronger, thus the absorption of FTO/0.3 mol% W-doped TiO_2 film is enhanced and the corresponding performances will be improved.

Since the PSCs have the structure of a planar heterojunction, it reveals a multi-layer structure, including FTO/W-doped TiO_2 (70 nm)/$Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})_3$(450 nm)/Spiro-OMeTAD (250 nm)/Au (70 nm). **Fig. 7a** shows the incident photon-to-electron conversion efficiency (IPCE) curves of pristine and 0.3mol% W-doped PSC. The IPCE curve shows a similar trend, but the intensity is different. The IPCE spectrum intensity of W-doped TiO_2 as the electron transport layer device is significantly improved across the whole wavelength. In

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comparison with the pristine TiO_2 (21.69 mA/cm^2), doped TiO_2 (23.3 mA/cm^2) has a higher integrated J_{sc} and corresponds to the J-V value. PSCs based on different concentrations of W-doped TiO_2 layer are fabricated and the performances of them are examined in **Table 1**. **Fig. 7b** shows the J-V curves of devices with different doping concentrations. Consequentially, the champion device, 0.3 mol% W-doped TiO_2 sample exhibits a better performance whose open-circuit voltage (V_{oc}) is 1.12 V, J_{sc} is 24.24 mA/cm^2, FF is 69.22%, and PCE is 18.85% when compared with the pristine TiO_2 sample. It is clearly noted that all the parameters are enhanced with the increased concentration of dopant since the increased density of active carrier, conductivity of the doped ETL and better E_g, E_f and CBM position of TiO_2. In terms of the substantial increase in J_{sc}, this improvement may be largely attribute to two factors: (1) The Fermi energy level has moved to conduction band side, which will improve the efficiency of electron injection; (2) With the higher conductivity of TiO_2 after doping W, more efficient charge will be extracted in the interface between TiO_2 and perovskite layer. Meanwhile, the higher V_{oc} may result from decreased charge recombination and modified charge gathering/separation. Interestingly, the performance of 0.5mol% W-doped TiO_2 is little worse than that of 0.3 mol% film, which could be ascribed to more electron defects formed and saturated electron barrier height owing to overdose doping. J-V curves were measured under reverse/forward scanning to analyze the hysteresis effect in **Fig. 7c**. **Table S3** summarizes the related parameters of the PSCs. It shows a hysteresis decrease after doping W in TiO_2. This improvement can be attributed to the

injection/separation of the effective carrier at the interface between ETL and perovskite layer. Therefore, W dopant plays as an important role in moderating the charge collection in the interface for ameliorating the hysteresis of PSCs.

The reproducibility of PSCs is studied through 35 individual devices based on the pristine and 0.3 mol% W-doped TiO_2. In **Fig. 8a and b**, the PCE value of W-doped device exhibits a more concentrated distribution when compared with undoped device. Statistical data of V_{oc}, J_{sc}, FF, and PCE are shown in **Fig. 8c, d, e and f**. In **Fig. S5**, we evaluated the device stability in the ambient air with a relative humidity of 36%. After 33 days exposure in the air, the W-doped device maintained about 80% of their initial PCE, which is higher than 60% of that for the control sample. The light stability was obtained in Fig. S6. In contrast, the PCE of 0.3 mol% W-doped TiO_2 PSC remained stable at more than half of its initial efficiency after 260 hours of exposure in a nitrogen atmosphere. This improved stability on PSCs is mainly attributed to the efficiently charge transfer between W-doped TiO_2 and perovskite layer, ameliorated conductivity of ETL, high quality of perovskite includes optimized crystallinity and large grain size by doping W dopant[75].

High efficiency perovskite solar cell based on tungsten-modified TiO_2 has been obtained. Then we use steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectra to further explain the charge transfer dynamics

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between perovskite and W-doped TiO_2, and analyze the underlying mechanism of efficiency improvement. In **Fig. 9a**, PL of perovskite films deposited on pure TiO_2 and 0.3 mol% W-doped TiO_2 are presented. Compared with the undoped sample, the photoluminescence intensity of the perovskite film on the W-doped TiO_2 was significantly reduced, shows more efficient PL quenching, indicating that electrons could be extracted and transported efficiently from the perovskite to the modified TiO_2[76]. Meanwhile, the doped device can effectively inhibit the carrier recombination at this interface. Furthermore, the TRPL curves (**Fig. 9b**) were shown to examine the charge excition lifetime by equation (3):

$$f(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) \tag{3}$$

Where τ_1 represents the fast decay time, τ_2 stands for the slow decay time and A is the coefficient of decay amplitude[77-80]. All fitted parameters are listed in **Table S4**. A strongly PL quenching was observed, and the average charge lifetime (τ_{ave}) has decreased from 102.49 ns to 31.17 ns with tungsten treatment. Therefore, with better electron extraction between the perovskite and TiO_2, electrons from the perovskite layer can be transfered efficient, and non-radiative composite defects are significantly reduced[81]. These properties are attributed to the reduction of defect state density and the formation of a good interface between perovskite and W-doped TiO_2.

In order to quantitatively analyze the density of defect states in perovskite films, we prepared the following device structures: FTO/TiO_2 (undoped or doped)/ Perovskite

/PCBM/Ag. We measured the device current-voltage curves under dark conditions (**Fig. 9c**), and then calculated the defect density (N_t) by space charge limited current method (SCLC). N_t is calculated by equation N_t:

$$N_t = 2\varepsilon_r \varepsilon_0 V_{TFL}/qL^2 \tag{4}$$

Where V_{TFL} is the trap-filled limit voltage, L stands for the thickness of perovskite layer (310 nm), e stands for the charge of electron and ε_r and ε_0 are the relative permittivity (28.8) and absolute permittivity (8.85×10^{-12} F/m), respectively[82]. It can be seen from the curve that the V_{TFL} decreases from 0.61V to 0.38 V; the calculated defect densities of pristine TiO_2 and 0.3 mol% W-doped device are 2.02×10^{16} cm^{-3} and 1.26×10^{16} cm^{-3}, correspondingly. This result directly proves tungsten doping can effectively passivate the defect of perovskite layer. It is consistent with the photoluminescence result.

Electrochemical impedance spectroscopy (EIS) was utilized to examine the mechanism of charge transfer. In **Fig. 9d**, low frequency curve represents the charge composition, usually representing the composite impedance, while the high frequency curve is related to the carrier transport impedance[83, 84]. According to the simulation data, the series resistance of W-doped device decreases, which may be ascribed to the fill factor of the devices has increased. The series resistance (R_s) and recombination resistance (R_{rec}) were measured by EIS system in **Table S5**. A lower value of R_s and larger value of R_{rec} were obtained in W-doped device, indicating the charge transfer rate has increased and the electron conductivity were improved. Consequently, these results

confirm that tungsten doping is conducive to perovskite solar cell.

4. Conclusions

In summary, W-doped TiO_2 layer, as ETL in PSCs, was fabricated successfully through the low-temperature solution-process. The PCE of improved device is 18.85%, which is almost 28.1% higher than that of pristine TiO_2 device (14.71%). It can be seen that improved conductivity of film, upshift of the E_f and lower defect density will efficiently increase injection/separation of the carrier at the TiO_2/perovskite layer interface. Therefore, J_{sc}, FF and stability are subsequently increased accordingly since the improvement for doping W element. Consequently, the proposed method using lower-valency materials as dopant, fabricated in low temperature, might provide an effective way for high-performance PSCs technology and potential application in wearable low-cost electronics.

References

[1] S.D. Stranks, G.E. Eperon, G. Grancini, C. Menelaou, M.J. Alcocer, T. Leijtens, L.M. Herz, A. Petrozza, H.J. Snaith, Electron-hole diffusion lengths exceeding 1 micrometer in an organometal trihalide perovskite absorber, Science, 342 (2013) 341-344

[2] G. Xing, N. Mathews, S. Sun, S.S. Lim, Y.M. Lam, M. Grätzel, S. Mhaisalkar, T.C. Sum, Long-range balanced electron-and hole-transport lengths in organic-inorganic CH3NH3PbI3, Science, 342 (2013) 344-347

[3] Y. Yuan, T. Li, Q. Wang, J. Xing, A. Gruverman, J. Huang, Anomalous photovoltaic effect in organic-inorganic hybrid perovskite solar cells, Science advances, 3 (2017) e1602164

[4] A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, Organometal halide perovskites as visible-light sensitizers for photovoltaic cells, Journal of the American Chemical Society, 131 (2009) 6050-6051

[5] X. Li, D. Bi, C. Yi, J.-D. Décoppet, J. Luo, S.M. Zakeeruddin, A. Hagfeldt, M. Grätzel, A vacuum flash–assisted solution process for high-efficiency large-area perovskite solar cells, Science, 353 (2016) 58-62

[6] Z. Wang, X. Zhu, S. Zuo, M. Chen, C. Zhang, C. Wang, X. Ren, Z. Yang, Z. Liu, X. Xu, 27%-Efficiency Four-Terminal Perovskite/Silicon Tandem Solar Cells by Sandwiched Gold Nanomesh, Advanced Functional Materials, 30 (2020) 1908298

[7] W.S. Yang, J.H. Noh, N.J. Jeon, Y.C. Kim, S. Ryu, J. Seo, S.I. Seok, High-performance photovoltaic perovskite layers fabricated through intramolecular exchange, Science, 348 (2015) 1234-1237

[8] G.E. Eperon, S.D. Stranks, C. Menelaou, M.B. Johnston, L.M. Herz, H.J. Snaith, Formamidinium lead trihalide: a broadly tunable perovskite for efficient planar heterojunction solar cells, Energy & Environmental Science, 7 (2014) 982-988.http://dx.doi.org/10.1039/C3EE43822H

[9] Y. Wu, A. Islam, X. Yang, C. Qin, J. Liu, K. Zhang, W. Peng, L. Han, Retarding the crystallization of PbI$_2$ for highly reproducible planar-structured perovskite solar cells via sequential deposition, Energy & Environmental Science, 7 (2014) 2934-2938.http://dx.doi.org/10.1039/C4EE01624F

[10] I. Zarazua, J. Bisquert, G. Garcia-Belmonte, Light-induced space-charge accumulation zone as photovoltaic mechanism in perovskite solar cells, The journal of physical chemistry letters, 7 (2016) 525-528

[11] B. Conings, L. Baeten, T. Jacobs, R. Dera, J. D'Haen, J. Manca, H.-G. Boyen, An easy-to-fabricate low-temperature TiO$_2$ electron collection layer for high efficiency planar heterojunction perovskite solar cells, APL Materials, 2 (2014) 081505

[12] D.W. Liu, Physics and Biology Collaborate to Color the World, CBE—Life Sciences Education, 12 (2013) 133-138

[13] W. Ke, G. Fang, Q. Liu, L. Xiong, P. Qin, H. Tao, J. Wang, H. Lei, B. Li, J. Wan, Low-temperature solution-processed tin oxide as an alternative electron transporting layer for efficient perovskite solar cells, Journal of the American Chemical Society, 137 (2015) 6730-6733

[14] M.H. Kumar, N. Yantara, S. Dharani, M. Graetzel, S. Mhaisalkar, P.P. Boix, N. Mathews, Flexible, low-temperature, solution processed ZnO-based perovskite solid state solar cells,

Chemical Communications, 49 (2013) 11089-11091.http://dx.doi.org/10.1039/C3CC46534A

[15] K. Wang, Y. Shi, B. Li, L. Zhao, W. Wang, X. Wang, X. Bai, S. Wang, C. Hao, T. Ma, Amorphous inorganic electron-selective layers for efficient perovskite solar cells: Feasible strategy towards room-temperature fabrication, Advanced Materials, 28 (2016) 1891-1897

[16] J. Ma, Z. Lin, X. Guo, L. Zhou, J. Su, C. Zhang, Z. Yang, J. Chang, S. Liu, Y. Hao, Low-temperature solution-processed ZnO electron transport layer for highly efficient and stable planar perovskite solar cells with efficiency over 20%, Solar RRL, 3 (2019) 1900096

[17] X. Huang, J. Du, X. Guo, Z. Lin, J. Ma, J. Su, L. Feng, C. Zhang, J. Zhang, J. Chang, Polyelectrolyte-doped SnO2 as a tunable electron transport layer for high-efficiency and stable perovskite solar cells, Solar RRL, 4 (2020) 1900336

[18] M. Yue, J. Su, P. Zhao, Z. Lin, J. Zhang, J. Chang, Y. Hao, Optimizing the performance of CsPbI$_3$-based perovskite solar cells via doping a ZnO electron transport layer coupled with interface engineering, Nano-Micro Letters, 11 (2019) 1-14

[19] B. Zhang, J. Su, X. Guo, L. Zhou, Z. Lin, L. Feng, J. Zhang, J. Chang, Y. Hao, NiO/perovskite heterojunction contact engineering for highly efficient and stable perovskite solar cells, Advanced Science, 7 (2020) 1903044

[20] J. Yu, Q. Li, J. Fan, B. Cheng, Fabrication and photovoltaic performance of hierarchically titanate tubular structures self-assembled by nanotubes and nanosheets, Chemical Communications, 47 (2011) 9161-9163.http://dx.doi.org/10.1039/C1CC12722E

[21] X. Zhu, B. Cheng, J. Yu, W. Ho, Halogen poisoning effect of Pt-TiO$_2$ for formaldehyde catalytic oxidation performance at room temperature, Applied Surface Science, 364 (2016) 808-814

[22] K. Lv, J. Yu, J. Fan, M. Jaroniec, Rugby-like anatase titania hollow nanoparticles with enhanced photocatalytic activity, CrystEngComm, 13 (2011) 7044-7048.http://dx.doi.org/10.1039/C1CE05907F

[23] J. Fan, L. Zhao, J. Yu, G. Liu, The effect of calcination temperature on the microstructure and photocatalytic activity of TiO$_2$-based composite nanotubes prepared by an in situ template dissolution method, Nanoscale, 4 (2012) 6597-6603.http://dx.doi.org/10.1039/C2NR32048G

[24] J.K. Kim, S.U. Chai, Y. Ji, B. Levy-Wendt, S.H. Kim, Y. Yi, T.F. Heinz, J.K. Nørskov, J.H. Park, X. Zheng, Resolving Hysteresis in Perovskite Solar Cells with Rapid Flame-Processed Cobalt-Doped TiO$_2$, Advanced Energy Materials, 8 (2018) 1801717

[25] J. Peng, T. Duong, X. Zhou, H. Shen, Y. Wu, H.K. Mulmudi, Y. Wan, D. Zhong, J. Li, T. Tsuzuki, Efficient indium-doped TiO$_x$ electron transport layers for high-performance perovskite solar cells and perovskite-silicon tandems, Advanced Energy Materials, 7 (2017) 1601768

[26] Y. Wu, X. Yang, H. Chen, K. Zhang, C. Qin, J. Liu, W. Peng, A. Islam, E. Bi, F. Ye, Highly compact TiO$_2$ layer for efficient hole-blocking in perovskite solar cells, Applied Physics Express, 7 (2014) 052301

[27] A. Kogo, Y. Sanehira, Y. Numata, M. Ikegami, T. Miyasaka, Amorphous metal oxide blocking layers for highly efficient low-temperature brookite TiO$_2$-based perovskite solar cells, ACS applied materials & interfaces, 10 (2018) 2224-2229

[28] K. Wang, Y. Shi, Q. Dong, Y. Li, S. Wang, X. Yu, M. Wu, T. Ma, Low-Temperature and

Solution-Processed Amorphous WO (x) as Electron-Selective Layer for Perovskite Solar Cells, The journal of physical chemistry letters, 6 (2015) 755-759

[29] A. Guerrero, G. Garcia-Belmonte, I. Mora-Sero, J. Bisquert, Y.S. Kang, T.J. Jacobsson, J.-P. Correa-Baena, A. Hagfeldt, Properties of contact and bulk impedances in hybrid lead halide perovskite solar cells including inductive loop elements, The Journal of Physical Chemistry C, 120 (2016) 8023-8032

[30] B.J. Kim, D.H. Kim, Y.-Y. Lee, H.-W. Shin, G.S. Han, J.S. Hong, K. Mahmood, T.K. Ahn, Y.-C. Joo, K.S. Hong, N.-G. Park, S. Lee, H.S. Jung, Highly efficient and bending durable perovskite solar cells: toward a wearable power source, Energy & Environmental Science, 8 (2015) 916-921.http://dx.doi.org/10.1039/C4EE02441A

[31] F. Di Giacomo, V. Zardetto, A. D'Epifanio, S. Pescetelli, F. Matteocci, S. Razza, A. Di Carlo, S. Licoccia, W.M. Kessels, M. Creatore, Flexible perovskite photovoltaic modules and solar cells based on atomic layer deposited compact layers and UV-irradiated TiO_2 scaffolds on plastic substrates, Advanced Energy Materials, 5 (2015) 1401808

[32] S.S. Mali, C.K. Hong, A. Inamdar, H. Im, S.E. Shim, Efficient planar nip type heterojunction flexible perovskite solar cells with sputtered TiO_2 electron transporting layers, Nanoscale, 9 (2017) 3095-3104

[33] D. Yang, R. Yang, J. Zhang, Z. Yang, S.F. Liu, C. Li, High efficiency flexible perovskite solar cells using superior low temperature TiO_2, Energy & Environmental Science, 8 (2015) 3208-3214

[34] A. Yella, L.-P. Heiniger, P. Gao, M.K. Nazeeruddin, M. Gra¨tzel, Nanocrystalline rutile electron extraction layer enables low-temperature solution processed perovskite photovoltaics with 13.7% efficiency, Nano letters, 14 (2014) 2591-2596

[35] J. Ma, X. Guo, L. Zhou, Z. Lin, C. Zhang, Z. Yang, G. Lu, J. Chang, Y. Hao, Enhanced planar perovskite solar cell performance via contact passivation of TiO_2/perovskite interface with NaCl doping approach, ACS Applied Energy Materials, 1 (2018) 3826-3834

[36] Z. Li, P. Wang, C. Ma, F. Igbari, Y. Kang, K.-L. Wang, W. Song, C. Dong, Y. Li, J. Yao, Single-Layered MXene Nanosheets Doping TiO_2 for Efficient and Stable Double Perovskite Solar Cells, Journal of the American Chemical Society, 143 (2021) 2593-2600

[37] Q.-Q. Ye, Z.-K. Wang, M. Li, C.-C. Zhang, K.-H. Hu, L.-S. Liao, N-type doping of fullerenes for planar perovskite solar cells, ACS Energy Letters, 3 (2018) 875-882

[38] M.C. Wu, Y.T. Lin, S.H. Chen, M.H. Jao, Y.H. Chang, K.M. Lee, C.S. Lai, Y.F. Chen, W.F. Su, Achieving High-Performance Perovskite Photovoltaic by Morphology Engineering of Low-Temperature Processed Zn-Doped TiO_2 Electron Transport Layer, Small, (2020) 2002201

[39] Z.K. Wang, L.S. Liao, Doped Charge-Transporting Layers in Planar Perovskite Solar Cells, Advanced Optical Materials, 6 (2018) 1800276

[40] X. Hou, J. Zhou, S. Huang, W. Ou-Yang, L. Pan, X. Chen, Efficient quasi-mesoscopic perovskite solar cells using Li-doped hierarchical TiO_2 as scaffold of scattered distribution, Chemical Engineering Journal, 330 (2017) 947-955

[41] D. Liu, S. Li, P. Zhang, Y. Wang, R. Zhang, H. Sarvari, F. Wang, J. Wu, Z. Wang, Z.D. Chen, Efficient planar heterojunction perovskite solar cells with Li-doped compact TiO_2 layer, Nano Energy, 31 (2017) 462-468

[42] J. Wang, M. Qin, H. Tao, W. Ke, Z. Chen, J. Wan, P. Qin, L. Xiong, H. Lei, H. Yu, Performance enhancement of perovskite solar cells with Mg-doped TiO_2 compact film as the hole-blocking layer, Applied Physics Letters, 106 (2015) 121104

[43] J. Hu, R. Gottesman, L. Gouda, A. Kama, M. Priel, S. Tirosh, J. Bisquert, A. Zaban, Photovoltage behavior in perovskite solar cells under light-soaking showing photoinduced interfacial changes, ACS Energy Letters, 2 (2017) 950-956

[44] H. Zhang, J. Shi, X. Xu, L. Zhu, Y. Luo, D. Li, Q. Meng, Mg-doped TiO_2 boosts the efficiency of planar perovskite solar cells to exceed 19%, Journal of Materials Chemistry A, 4 (2016) 15383-15389.http://dx.doi.org/10.1039/C6TA06879K

[45] M.-C. Wu, S.-H. Chan, M.-H. Jao, W.-F. Su, Enhanced short-circuit current density of perovskite solar cells using Zn-doped TiO_2 as electron transport layer, Solar Energy Materials and Solar Cells, 157 (2016) 447-453

[46] S.K. Pathak, A. Abate, P. Ruckdeschel, B. Roose, K.C. Gödel, Y. Vaynzof, A. Santhala, S.I. Watanabe, D.J. Hollman, N. Noel, Performance and stability enhancement of dye-sensitized and perovskite solar cells by Al doping of TiO_2, Advanced Functional Materials, 24 (2014) 6046-6055

[47] S. Wang, B. Liu, Y. Zhu, Z. Ma, B. Liu, X. Miao, R. Ma, C. Wang, Enhanced performance of TiO_2-based perovskite solar cells with Ru-doped TiO_2 electron transport layer, Solar Energy, 169 (2018) 335-342

[48] B. Roose, S. Pathak, U. Steiner, Doping of TiO_2 for sensitized solar cells, Chemical Society Reviews, 44 (2015) 8326-8349

[49] M. Yang, R. Guo, K. Kadel, Y. Liu, K. O'Shea, R. Bone, X. Wang, J. He, W. Li, Improved charge transport of Nb-doped TiO_2 nanorods in methylammonium lead iodide bromide perovskite solar cells, Journal of Materials Chemistry A, 2 (2014) 19616-19622

[50] H. Zhou, Q. Chen, G. Li, S. Luo, T.-b. Song, H.-S. Duan, Z. Hong, J. You, Y. Liu, Y. Yang, Interface engineering of highly efficient perovskite solar cells, Science, 345 (2014) 542-546

[51] J.A. Dorman, J. Weickert, J.B. Reindl, M. Putnik, A. Wisnet, M. Noebels, C. Scheu, L. Schmidt-Mende, Control of recombination pathways in TiO_2 nanowire hybrid solar cells using Sn^{4+} dopants, The Journal of Physical Chemistry C, 118 (2014) 16672-16679

[52] J. Liu, J. Zhang, G. Yue, X. Lu, Z. Hu, Y. Zhu, W-doped TiO_2 photoanode for high performance perovskite solar cell, Electrochimica Acta, 195 (2016) 143-149

[53] Y. Xiao, N. Cheng, K.K. Kondamareddy, C. Wang, P. Liu, S. Guo, X.-Z. Zhao, W-doped TiO_2 mesoporous electron transport layer for efficient hole transport material free perovskite solar cells employing carbon counter electrodes, Journal of Power Sources, 342 (2017) 489-494

[54] Y. You, W. Tian, L. Min, F. Cao, K. Deng, L. Li, TiO_2/WO_3 bilayer as electron transport layer for efficient planar perovskite solar cell with efficiency exceeding 20%, Advanced Materials Interfaces, 7 (2020) 1901406

[55] J. Zhang, C. Shi, J. Chen, Y. Wang, M. Li, Preparation of ultra-thin and high-quality WO_3 compact layers and comparision of WO_3 and TiO_2 compact layer thickness in planar perovskite solar cells, Journal of Solid State Chemistry, 238 (2016) 223-228

[56] K. Mahmood, B.S. Swain, A.R. Kirmani, A. Amassian, Highly efficient perovskite solar cells based on a nanostructured WO_3–TiO_2 core–shell electron transporting material, Journal of

Materials Chemistry A, 3 (2015) 9051-9057

[57] K. Wang, Y. Shi, L. Gao, R. Chi, K. Shi, B. Guo, L. Zhao, T. Ma, W (Nb) Ox-based efficient flexible perovskite solar cells: From material optimization to working principle, Nano Energy, 31 (2017) 424-431

[58] Y. Hou, C.O.R. Quiroz, S. Scheiner, W. Chen, T. Stubhan, A. Hirsch, M. Halik, C.J. Brabec, Low-Temperature and Hysteresis-Free Electron-Transporting Layers for Efficient, Regular, and Planar Structure Perovskite Solar Cells, Advanced Energy Materials, 5 (2015) 1501056

[59] V.O. Eze, Y. Seike, T. Mori, Efficient planar perovskite solar cells using solution-processed amorphous WO_x/fullerene C_{60} as electron extraction layers, Organic Electronics, 46 (2017) 253-262

[60] T. Wu, J. Wu, Y. Tu, X. He, Z. Lan, M. Huang, J. Lin, Solvent engineering for high-quality perovskite solar cell with an efficiency approaching 20%, Journal of Power Sources, 365 (2017) 1-6

[61] L. Wang, Z. Yuan, T.A. Egerton, Comparison of nano-particulate TiO_2 prepared from titanium tetrachloride and titanium tetraisopropoxide, Materials Chemistry and Physics, 133 (2012) 304-310

[62] M. Ratova, G.T. West, P.J. Kelly, Optimization studies of photocatalytic tungsten-doped titania coatings deposited by reactive magnetron co-sputtering, Coatings, 3 (2013) 194-207

[63] X. Zhang, F. Liu, Q.-L. Huang, G. Zhou, Z.-S. Wang, Dye-sensitized W-doped TiO_2 solar cells with a tunable conduction band and suppressed charge recombination, The Journal of Physical Chemistry C, 115 (2011) 12665-12671

[64] J. Gong, W. Pu, C. Yang, J. Zhang, Tungsten and nitrogen co-doped TiO_2 electrode sensitized with Fe–chlorophyllin for visible light photoelectrocatalysis, Chemical engineering journal, 209 (2012) 94-101

[65] S. Liu, E. Guo, L. Yin, Tailored visible-light driven anatase TiO_2 photocatalysts based on controllable metal ion doping and ordered mesoporous structure, Journal of Materials Chemistry, 22 (2012) 5031-5041

[66] S. Thogiti, J.Y. Park, C.T. Thanh Thuy, D.K. Lee, B.-K. Min, H.J. Yun, J.H. Kim, High-performance dye-sensitized solar cells through graded electron transport in band-engineered W-TiO_2 cascade layer, ACS Sustainable Chemistry & Engineering, 6 (2018) 13025-13034

[67] S.A.K. Leghari, S. Sajjad, J. Zhang, Large mesoporous micro-spheres of WO_3/TiO_2 composite with enhanced visible light photo activity, RSC advances, 3 (2013) 15354-15361

[68] B. Zhu, P. Xia, Y. Li, W. Ho, J. Yu, Fabrication and photocatalytic activity enhanced mechanism of direct Z-scheme g-C_3N_4/Ag_2WO_4 photocatalyst, Applied Surface Science, 391 (2017) 175-183

[69] J. Gong, C. Yang, W. Pu, J. Zhang, Liquid phase deposition of tungsten doped TiO_2 films for visible light photoelectrocatalytic degradation of dodecyl-benzenesulfonate, Chemical Engineering Journal, 167 (2011) 190-197

[70] D.-m. Chen, G. Xu, L. Miao, L.-h. Chen, S. Nakao, P. Jin, W-doped anatase TiO_2 transparent conductive oxide films: Theory and experiment, Journal of Applied Physics, 107 (2010) 063707

[71] J. Obrzut, K.A. Page, Electrical conductivity and relaxation in poly (3-hexylthiophene),

Physical Review B, 80 (2009) 195211

[72] A.M. Goodman, A. Rose, Double extraction of uniformly generated electron-hole pairs from insulators with noninjecting contacts, Journal of Applied Physics, 42 (1971) 2823-2830

[73] K.A. Bhabu, J. Theerthagiri, J. Madhavan, T. Balu, G. Muralidharan, T. Rajasekaran, Cubic fluorite phase of samarium doped cerium oxide (CeO_2) 0.96 Sm 0.04 for solid oxide fuel cell electrolyte, Journal of Materials Science: Materials in Electronics, 27 (2016) 1566-1573

[74] S.G. Kim, M.J. Ju, I.T. Choi, W.S. Choi, H.-J. Choi, J.-B. Baek, H.K. Kim, Nb-doped TiO_2 nanoparticles for organic dye-sensitized solar cells, Rsc Advances, 3 (2013) 16380-16386

[75] T. Leijtens, G.E. Eperon, N.K. Noel, S.N. Habisreutinger, A. Petrozza, H.J. Snaith, Stability of metal halide perovskite solar cells, Advanced Energy Materials, 5 (2015) 1500963

[76] J. Peng, Y. Wu, W. Ye, D.A. Jacobs, H. Shen, X. Fu, Y. Wan, N. Wu, C. Barugkin, H.T. Nguyen, Interface passivation using ultrathin polymer–fullerene films for high-efficiency perovskite solar cells with negligible hysteresis, Energy & Environmental Science, 10 (2017) 1792-1800

[77] S. Yuan, F. Qian, S. Yang, Y. Cai, Q. Wang, J. Sun, Z. Liu, S. Liu, NbF5: A Novel α-Phase Stabilizer for FA-Based Perovskite Solar Cells with High Efficiency, Advanced Functional Materials, 29 (2019) 1807850

[78] H. Chen, T. Liu, P. Zhou, S. Li, J. Ren, H. He, J. Wang, N. Wang, S. Guo, Efficient Bifacial Passivation with Crosslinked Thioctic Acid for High-Performance Methylammonium Lead Iodide Perovskite Solar Cells, Advanced Materials, 32 (2020) 1905661

[79] S. Yang, H. Zhao, M. Wu, S. Yuan, Y. Han, Z. Liu, K. Guo, S.F. Liu, S. Yang, H. Zhao, Highly efficient and stable planar CsPbI2Br perovskite solar cell with a new sensitive-dopant-free hole transport layer obtained via an effective surface passivation, Solar Energy Materials and Solar Cells, 201 (2019) 110052

[80] F. Wei, B. Jiao, H. Dong, J. Xu, T. Lei, J. Zhang, Y. Yu, L. Ma, D. Wang, J. Chen, Bifunctional π-conjugated ligand assisted stable and efficient perovskite solar cell fabrication via interfacial stitching, Journal of Materials Chemistry A, 7 (2019) 16533-16540

[81] C. Fei, B. Li, R. Zhang, H. Fu, J. Tian, G. Cao, Highly efficient and stable perovskite solar cells based on monolithically grained $CH_3NH_3PbI_3$ film, Advanced Energy Materials, 7 (2017) 1602017

[82] Q. Dong, Y. Fang, Y. Shao, P. Mulligan, J. Qiu, L. Cao, J. Huang, Electron-hole diffusion lengths> 175 μm in solution-grown $CH_3NH_3PbI_3$ single crystals, Science, 347 (2015) 967-970

[83] N. Li, Z. Zhu, C.C. Chueh, H. Liu, B. Peng, A. Petrone, X. Li, L. Wang, A.K.Y. Jen, Mixed cation FAxPEA1−xPbI3 with enhanced phase and ambient stability toward high-performance perovskite solar cells, Advanced Energy Materials, 7 (2017) 1601307

[84] J.C. Yu, D.B. Kim, G. Baek, B.R. Lee, E.D. Jung, S. Lee, J.H. Chu, D.K. Lee, K.J. Choi, S. Cho, High-Performance Planar Perovskite Optoelectronic Devices: A Morphological and Interfacial Control by Polar Solvent Treatment, Advanced Materials, 27 (2015) 3492-3500