Temperature effect of the compact TiO₂ layer in planar perovskite solar cells: An interfacial electrical, optical and carrier mobility study

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Abstract

The power conversion efficiency of TiO₂ based organo-lead halide perovskite solar cells has already surpassed 20% by utilizing low temperature solution processing techniques. However, the electrostatic structures and exciton/electron transport mechanisms at the TiO₂/perovskite interface are not fully understood. In this report, simple planar TiO₂/perovskite heterojunctions are fabricated with different TiO₂ compact layers followed by studies of their effect on the charge extraction/transport properties of the deposited heterojunctions. Efficient perovskite solar cells based on these TiO₂/perovskite heterojunctions [with CH₃NH₃PbI₃ and FA₀.₈₁MA₀.₁₅Pb(I₀.₈₃₆Br₀.₁₅)₃ films] have been fabricated and the devices exhibit reproducible efficiency values and good stability. The impact of interfacial potential barrier and TiO₂ surface properties on photogenerated carrier transport mechanisms and overall power conversion efficiency of perovskite solar cells is investigated by using comprehensive electrical and optical characterization methods such as SEM, XRD, XPS, Raman spectroscopy, TRPL, TAS and TPD. Obtained results indicate that efficient device can be fabricated by optimizing of TiO₂ annealing conditions.

1. Introduction

Lead trihalide perovskites combined with various functional layers have attracted intense attention for excellent optoelectronic device applications such as solar cell due to their large absorption coefficient, long carrier lifetime and diffusion length [1–12]. In order to achieve high efficiency in perovskite solar cells (PSCs), the properties of perovskite materials and device fabrication techniques are being subjects of continuous optimization efforts, however, the TiO₂ compact layer (CL) and electron transporting layer made from typical sol-gel technique are predominantly utilized in fabrication of highly efficient PSCs [1,6–12]. Power conversion efficiencies (PCEs) of TiO₂ based PSCs have increased rapidly from around 10% in the early publications to above 22.1% in recent reports [1,2,10,11], suggesting that TiO₂ is a promising electron transport material for high efficiency PSCs. Furthermore, the TiO₂ layer works together with the perovskite layer in efficient PSCs and its main functions are to transport charge carriers (electrons) and prevent recombination with electron. Even though electron transport mechanism at the TiO₂/perovskite interface has been a topic of previous studies [12,13], details on electron transfer as well as atomic/electronic structures present at such interfaces are still not fully revealed, especially at different types of TiO₂ CL/perovskite heterojunctions fabricated using variations in TiO₂ structure such as introduction of oxygen vacancies and additives (carbon materials and organic polymers) [10]. The oxygen vacancies and additives are various for TiO₂ compact layer made from sol-gel technology with different annealing temperatures. Hence, systematical investigation the temperature effect of the compact TiO₂ layer is of crucial importance for development of efficient planar PSCs.

In this system, trihalide perovskite materials, such as methylammonium lead iodide (CH₃NH₃PbI₃) as well as formamidinium lead iodide (HC(NH₂)₂PbI₃) and methylammonium lead bromide (CH₃NH₂PbBr₃) mixed halides (in this study, FA₀.₈₁MA₀.₁₅Pb(I₀.₈₃₆Br₀.₁₅)₃ was used), are utilized to fabricate per-
ovskite solar cells based on different TiO2 layers with some standard processes [1,14–16]. Comprehensive investigations on the structural, optical and electrical properties of TiO2/CH3NH3PbI3 interfaces were operated. Detailed carrier transport processes at various TiO2/CH3NH3PbI3 interfaces and complete PSCs were observed for the first time. Strong interface dipole effect [12,13] (potential interface barrier) was also found at the TiO2/CH3NH3PbI3 interface and the formation mechanism was explored. Interfacial potential barrier and TiO2 surface defects (organic residue, degree of crystallinity and oxygen vacancies density) could affect the charge carrier transporting process and lead to current-voltage curve hysteresis [9,12,13] and further influence the efficiency of the TiO2 based PSCs.

2. Methods

2.1. Substrate preparation

Quartz and fluoride-doped tin oxide (FTO) glass substrates were cleaned by ultrasonication with detergent, de-ionized water, acetone (Sigma) and isopropanol (Sigma) and finally treated under an UV ozone treatment for 10 min at 100 °C to remove the last traces of organic residues.

2.2. TiO2 coated FTO/quartz samples fabrication

To prepare the TiO2 flat film precursor solution, titanium isopropoxide (1 mL, Sigma) and 12 M HCl solution (10 mL, Sigma) were diluted in ethanol (10 mL, Sigma). Solution was filtered with a PTFE filter with 0.2 μm pore size before use. The cleaned FTO/quartz substrates were spin-coated the TiO2 film precursor solution (35 μL) at 5000 rpm for 30 s and consequently dried at 120 °C for 10 min in a N2 glovebox. Subsequently, they were gradually annealed at 300, 400 and 500 °C for 30 min in air in a calibrated furnace (Lindberg) with an acceleration of 5 °C/min, separately. Some obtained TiO2 samples were stored at N2 filled glove box for 20 days in order to examine surface adsorption behaviour.

2.3. Solar cell fabrication

0.100g CH3NH3I (Dyesol) was mixed with 0.289g PbI2 (99.999% Sigma) in 0.5 mL anhydrous N,N-dimethylformamide (Sigma) by magnetic stirring for 30 min to produce a clear CH3NH3PbI3 precursor solution with concentration of 45 wt%. To deposit perovskite films, the stock solution was quickly dropped onto the substrate and spun at 4000 rpm and after three or four seconds, chlorobenzene (110 mL) was dropped in 0.4 mL anhydrous N,N-dimethylformamide and 0.1 mL anhydrous dimethylsulfoxide (Sigma). The spin-coating procedure was performed in an N2 filled glovebox: first, 2000 rpm for 10 s; second, 6000 rpm for 30 s, then anhydrous chlorobenzene (110 mL) was dropped in 8–10 s during the 6000 rpm spin-coating process. The substrate was then heated on a hotplate at 100 °C for 60 min.

2.4. Characterization

Current-voltage characteristics were measured in an inert environment (MBraun glovebox, N2 atmosphere) conditions using a solar simulator (SAN-El Electric XES-301S 300 W Xe Lamp JIS Class AAA) and a Keithley 2400 sourcemeter. The cell area under test was defined with a 0.09 cm2 aperture in a metal mask. IPCE as a function of light wavelength was measured with a home-built setup consisting of an Oriel 300-W Xe lamp in combination with an Oriel Cornerstone 130 monochromator and a SRS 810 lock-in amplifier (Stanford Research Systems). The number of photons incident on the device was calculated for each wavelength by using a calibrated Si diode as the reference. IPCE photocurrents were recorded under short-circuit conditions using a Keithley 2400 sourcemeter. The surface and cross section morphologies of perovskite films and entire PSCs were investigated by using a scanning electron microscope (SEM, JEOL JSM-7001F) at 10 kV. X-ray diffraction (XRD) experiments were conducted by a Bruker AXS (D8 ADVANCE) X-ray diffractometer with Cu Kα radiation (λ=1.54 Å).

X-ray photoelectron spectroscopy (XPS) was performed on the samples in a custom-made UHV multi-channel system with base pressure better than 1×10−9 Torr. The XPS source is monochromatic Al Kα with photon energy at 1486.7 eV. The photoelectrons are measured by an electron analyzer (Omicron EA125). The optical phonon characteristics of TiO2 samples were studied using Raman spectroscopy by using a HORIBA Jobin Yvon T64000 system and 514.5 nm laser line. The ultraviolet-visible (UV–vis) spectra were measured on a PerkinElmer Lambda 950 UV/VIS/NIR spectrometer. The 440 nm line of a picosecond pulsed laser diode (PicoQuant PDL 800-8-B) was used as the excitation light-source for the time-resolved photoluminescence (TRPL) experiments; and the PL decays were recorded by a time-correlated single-photon counting module and a picosecond event timer (PicoHarp 300). Transient absorption (TA) measurements were performed using Edinburg Laser Flash photolyispectrometer (LP920-KS). The sample was excited using a flash lamp pumped Q-switched Nd:YAG laser operating in third harmonic mode of wavelength 440 nm (Ekspla NT 341A) and the absorption/emission spectra were measured using an i-CCD (Andor). Small perturbation transient photovoltage decay (TPD) experiments were performed by using a Nd:YAG pulsed laser (EKSPLA NT341A-10-AW, pulse duration < 4 ns), as excitation light source (532 nm). The power intensity of the laser was adjusted by using neutral density filters to afford a small perturbation of the cell photovoltage (~20 mV). A white light halogen lamp and neutral density filters were employed to vary the back illumination level. The TPDs were monitored by using a custom setup consisting of digital oscilloscope (Agilent 54845A).

3. Results and discussion

3.1. XRD results

The X-ray diffraction (XRD) patterns of CH3NH3PbI3 films different TiO2 compact layers are shown in Fig. 1. The peak positions at 14.1°, 28.4°, 31.7° belong to the (110), (220), (310) faces of the prepared CH3NH3PbI3 crystals, respectively [2–5]. However, the peak intensity of 300 °C sample is lower than that of the 400 °C and 500 °C samples, indicating a less complete conversion of TiO2 precursor into TiO2 crystal in the low temperature sample. For 400 °C and 500 °C annealed TiO2 CLs, the organic parts in the precursor solution has been
burnt out and the crystallinity of these TiO2 samples are higher than that of the low temperature one. Apparently, CH3NH3PbI3 is much easier to growth on the TiO2 surfaces with relatively high crystallinity.

3.2. Morphology analysis

Usually, a flat and mirror-like CH3NH3PbI3 film can be deposited on a newly fabricated TiO2 CL (Fig. S1a, b). Relatively large size (300–400 nm) CH3NH3PbI3 crystals can be seen in this sample, which is benefit for high efficiency obtaining [6,7,10]. However, some nest-shaped structures were observed on the surface of deposited perovskite layer on top of a TiO2 CL which has been stored in a nitrogen filled glovebox for 20 days (Fig. S1c), the same image appeared in the other two samples having the same storage condition. The low crystallinity degree, incomplete transformation of TiO2 precursor (300 °C sample) and the oxygen vacancies (400 °C and 500 °C samples) in these TiO2 samples could induce gas and (or) dust absorption at the TiO2 surfaces [9,14,21] which would lead to the low affinity of top CH3NH3PbI3 layers resulting in formation of abovementioned perovskite nests. These structures might also prevent the carrier transporting at the TiO2/CH3NH3PbI3 interface, suggesting that storage of annealed TiO2 substrates should be avoided.

3.3. XPS results

XPS measurement were conducted to explore atomic and electronic structures of TiO2/perovskite heterojunctions, yielding results depicted in Figs. 2 and 3. Fig. 2 shows the XPS wide scan (Fig. 2a) and elemental spectra (Fig. 2b) of the prepared CH3NH3PbI3 sample on top of a 400 °C TiO2 CL sample. The binding energies peaks at 138.06 eV, 402.1 eV and 618.9 eV belong to Pb 4f, N 1s, and I 3d, which is in good agreement with some previous results [12,17], indicating the conversion of perovskite precursor into CH3NH3PbI3. According to some recent publications [18–20], the binding energy peaks of the XPS elemental spectra (Fig. 3a–c) of the different TiO2 layers show that the TiO2 precursor was successfully transformed into TiO2 in all the three samples. The slight difference of some characteristic peak (C 1s, N 1s, O 1s and Ti 2p) positions arose from the difference in surface and crystallinity conditions [21]. The organic compounds in the precursor were evaporated and the TiO2 precursor transformed to TiO2 completely at 400 °C and 500 °C, while some organic residues still be found in 300 °C sample because of the 288.6 eV binding energy peak in the C 1s XPS elemental spectrum (Fig. 3a). This binding energy could refer to carboxylate carbon, which indicated the presence of organic residues [22]. The O 1s XPS spectrum peak is shown in Fig. 3b, and the O 1s core levels show a slightly asymmetric shape near 531 eV and can be fitted well by two asymmetric Gaussian curves which are denoted as 530 eV and 531 eV peaks, respectively. The first binding energy could be ascribed to the oxygen atoms of TiO2 and the latter one was assigned to the hydroxyl groups, chemisorbed oxygen and/or organic oxygen on the surface of the sample [23,24]. Residual organic compounds in 300 °C sample and high density oxygen vacancies in 500 °C sample would absorb gas molecules and solid dusts [9,14,21], which is verified by the N 1s XPS spectra. According to Fig. 3c, the 300 °C sample surface absorbed most nitrogen compounds (such as NO and NH3) while the 400 °C sample absorbed the least.

3.4. Raman spectroscopy

Usually, the sol-gel method could induce defects such as oxygen vacancies in TiO2 and the number of oxygen vacancies in anatase TiO2 increased with annealing temperature [22,23]. The Raman spectra of various TiO2 samples were recorded to study the oxygen vacancies at the TiO2 surface. Generally, anatase TiO2 showed six different phonon vibration modes at 142, 197, 399, 515, 519 and 639 cm−1, which were attributed to 3Eg, 1A1g and 2B1g vibration modes respectively [23]. As can been seen in Fig. 3d, all the six characteristic peaks can be only found in 500 °C TiO2 sample which means the crystallinity in this sample is higher than that in the 300 °C and 400 °C samples; the Raman spectra also reveals broadening of 144, 397, 512 and 637 cm−1 peaks in the TiO2 samples as the annealing temperature increases from 300 °C to 500 °C. This peak broadening arose mainly owing to increase of oxygen vacancies especially at the surface [23].
3.5. Optical results

Optical properties of prepared samples were examined using ultraviolet visible (UV–vis) absorption, Time-resolved PL and transient absorption (TA) methods. UV–vis spectra of TiO2/CH3NH3PbI3 heterojunction samples are shown in Fig. 4a, the CH3NH3PbI3 perovskite film deposited on the TiO2 CLs shows a remarkable enhancement in the optical absorption spectra, which increases regularly with increasing the temperature. The UV–vis spectra for TiO2 samples are also recorded (see Fig. S2a in the Supporting information). A sharp negative band peaking around 760 nm (PB) together with a broad positive band at 550 nm (PA), peaking to the photobleaching of the band gap or exciton transition, whereas the positive band represents a photoinduced absorption (completed spectra see Fig. S3a in the Supporting information) [25]. The TA measurements on TiO2 samples were also attempted but the signals were too weak to be obtained (see Fig. S3b in the Supporting information). As illustrated in Fig. 4b, the bandaged PL decay spectra of all four CH3NH3PbI3 samples can be well-fitted with quadratic functions. Results can be interpreted in the following way: in the steady states, there were some surface states and many photodoped charges (holes) already existed in the perovskite samples. Once the concentration of photogenerated charge carriers from the laser pulse becomes comparable or greater than intrinsic hole density, recombination process transitions from monomolecular to bimolecular, resulting in formation of trap levels within crystal structure [26–28]. So the faster lifetime \( \tau_1 \) corresponded to the carrier-trapping decay [26,27]. A PL lifetime \( \tau_1 \) enhancement can be observed in TiO2/CH3NH3PbI3 samples compared to the bare CH3NH3PbI3 sample, particular in the 400 °C samples (Table 1). More precisely, The PL decay lifetime \( \tau_1 \) for 300 °C, 400 and 500 °C samples were 2.43, 3.30 and 2.40 ns, respectively, and a decreased lifetime 2.07 ns for pristine CH3NH3PbI3 sample. Generally, shorter PL lifetime corresponds to a faster excitons/carriers recombination/trapping/transporting process due to increase in recombination sites and (or) transport pathways within the sample [27]. The PL lifetime \( \tau_1 \) enhancement indicated that the TiO2 CLs might decrease the density of crystal defects in the deposited CH3NH3PbI3 layer. The PL lifetime \( \tau_2 \) of the TiO2/CH3NH3PbI3 samples were shorter than the pristine CH3NH3PbI3 sample with 41.16 ns (Table 1). We describe this behaviour as: TiO2 and CH3NH3PbI3 were novel semiconductor materials, a built-in energy level difference [10] could be generated when they contacted with each other, this energy level difference could induce the photogenerated carriers transporting from perovskite layer to TiO2 layer, resulting in a decreased lifetime (PL quenching) [12]. However, the recorded PL lifetime [12,25] (below 5 ns) of some hole-transporting materials (spiro-MeOTAD and Phenyl-C61-butyric acid methyl ester)/CH3NH3PbI3 bi-layers were significantly shorter than that \( \tau_2 \) of these CH3NH3PbI3/TiO2 samples. As can be seen from Table 1, the PL lifetime \( \tau_2 \) increased from 22.56 ns (300 °C sample) to 32.74 ns (400 °C sample) and then decreased to 30.57 ns (500 °C sample). This lifetime enhancement (compared to HTM/CH3NH3PbI3 heterojunctions) indicated strong presence of electron coupling between TiO2 and CH3NH3PbI3 at the interface revealing details about electron transport. Namely, movement of photogenerated carriers through
CH$_3$NH$_3$PbI$_3$/TiO$_2$ interface by charge transfer pathways can be retarded through mutual passivation between perovskite and inorganic oxide through formation of interfacial dipoles causing accumulation of charge carriers at the interface [12]. The PL decay experimental results in this report were verified by the results of TA decay experiments (Table 1). Unfortunately, the time resolution of ns-TA decay measurement is not enough to determine the faster decay component ($\tau_1$). However, it makes full sense that faster free carriers recombination process happened at 300 °C and 500 °C samples. More precisely, the TA lifetime decreased from 19 ns of 400 °C TiO$_2$/CH$_3$NH$_3$PbI$_3$ sample to 18 ns of 500 °C TiO$_2$/CH$_3$NH$_3$PbI$_3$ sample and end at 16 ns of 300 °C TiO$_2$/CH$_3$NH$_3$PbI$_3$ sample. The PL decay lifetime of various TiO$_2$ samples were very short (below 2 ns) when compared with the heterojunction samples, implying that the difference in PL lifetime in heterojunction samples derived from different electron transport mechanisms at the TiO$_2$/CH$_3$NH$_3$PbI$_3$ interfaces not from TiO$_2$ CL or CH$_3$NH$_3$PbI$_3$ layer. In other words, the surface states in CH$_3$NH$_3$PbI$_3$ and TiO$_2$ would passivate with each other and result in the interfacial dipoles (potential interfacial barrier). This potential interfacial barrier could affect the photogenerated electron transport from CH$_3$NH$_3$PbI$_3$ to TiO$_2$ and lead to the current voltage hysteresis of planar PSCs [12,13].

### 3.6. Devices performance and TPD results

Planar PCSs with same TiO$_2$/CH$_3$NH$_3$PbI$_3$ heterojunctions were fabricated. Firstly, the FTO glass substrates were covered with a 40 nm TiO$_2$ CL. After annealing at 300 °C, 400 °C and 500 °C, the light harvester-CH$_3$NH$_3$PbI$_3$, was then deposited. After annealing at 100 °C for 10 min, the p-type HTM spiro-MeOTAD was deposited to efficiently block contact between CH$_3$NH$_3$PbI$_3$ and Au. Gold electrodes were used to finalize devices rather than silver in order to avoid formation shunting paths with the TiO$_2$ in the absence of oxygen. Moreover, contact between silver electrode and lead halide film may trigger corrosion process [9,29]. The cross-section image of an optimized solar cell configuration can be seen in Fig. S1d. As depicted in Fig. 5a and b and Table 2, standard device where TiO$_2$ was annealed at 400 °C exhibited the largest short circuit current density ($J_{sc}$) of 22.00 mA cm$^{-2}$, an open-circuit voltage ($V_{oc}$) of 0.99 V, fill factor (FF) of 0.68 and overall PCE of 14.9%; for 300 °C sample, $J_{sc}$ of 9.80 mA cm$^{-2}$, $V_{oc}$ of 0.91 V, FF of 0.47 and PCE of 4.2%; for 500 °C sample: $J_{sc}$ of 21.00 mA cm$^{-2}$, $V_{oc}$ of 1.01 V, FF of 0.67 and PCE of 14.3% and all the J-V curves were obtained under simulated 1 sun illumination. A preliminary stability investigation of these perovskite solar cells have been operated in 40 days which shows that the devices stored in the dark at room temperature are relatively stable, with a PCE drop of only 0.7% during this period (as can be seen in Table S1). A histogram of 50 devices (Fig. S4) indicates good performance reproducibility of this kind of perovskite solar cell, with an average PCE of 14.9%. It was observed that the $V_{oc}$ is increasing with the increase of the annealing temperature which can be attributed to the high crystallinity of the TiO$_2$ sample treated with high temperature. A significant $J_{sc}$ fluctuation found among these devices can be ascribed to different charge carrier transport mechanisms at the TiO$_2$/CH$_3$NH$_3$PbI$_3$ interfaces. The longest PL lifetime ($\tau_2$) and the highest PCE were found in the samples calcinated at 400 °C TiO$_2$, as clearly shown in Fig. 5d, due to the accumulation of the photogenerated electrons in the active layer without trapping at the interface, generating sufficient time needed to

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**Table 1**

<table>
<thead>
<tr>
<th>CH$_3$NH$_3$PbI$_3$ samples</th>
<th>PL decays</th>
<th>TA decays</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\tau_1$ (ns)</td>
<td>$\tau_2$ (ns)</td>
</tr>
<tr>
<td>300 °C TiO$_2$/CH$_3$NH$_3$PbI$_3$</td>
<td>2.43</td>
<td>22.56</td>
</tr>
<tr>
<td>400 °C TiO$_2$/CH$_3$NH$_3$PbI$_3$</td>
<td>3.30</td>
<td>32.74</td>
</tr>
<tr>
<td>500 °C TiO$_2$/CH$_3$NH$_3$PbI$_3$</td>
<td>2.40</td>
<td>30.57</td>
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<tr>
<td>Glass/CH$_3$NH$_3$PbI$_3$</td>
<td>2.07</td>
<td>41.16</td>
</tr>
</tbody>
</table>

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Fig. 4. Results of various optical measurements. (a) Absorption spectra of TiO$_2$/CH$_3$NH$_3$PbI$_3$ samples. (b) PL decays (dots) and (c) TA decays (dots) and corresponding fitting curves (solid lines) of plain CH$_3$NH$_3$PbI$_3$ and TiO$_2$/CH$_3$NH$_3$PbI$_3$ samples.
overcome the interface potential barrier and contribute to current density. As for devices fabricated using 300 °C TiO2, surface defects and organic compounds could trap the accumulated carriers at the interface and contribute to the shortest PL lifetime (τ2) and lowest PCE in the device (Fig. 5c), carrier trapping process also (free electrons trapped by oxygen vacancies) happened at 500 °C TiO2 sample (Fig. 5e). It should be noted that presence of hysteresis effect is minimal or even negligible for the PSCs with mesoporous TiO2 layers according to recent publications [12,13]. The surface area of these nanoscale mesoporous TiO2 was much larger than planar TiO2 resulting in the increase of photogenerated carrier pathways at the TiO2 surface, so the interfacial accumulation effect of charge carriers in the active layer is suppressed and carriers can across the interface smoothly through these pathways.

In addition to the very slow decay, faster decay components occur as observed by small perturbation TPD [26,30,31], with time relaxation constant in the μs scale. Therefore, we operated complementary small perturbation TPDs by using a white light source to vary the back illumination level and a ns-pulsed 532 nm Nd/YAG laser to promote the voltage perturbation, and the results of 300 °C and 400 °C samples are shown in Fig. 6a and b respectively. The TPD shows two components of the decay, τ1 and τ2, that span from 10 μs to 160 μs. We can clearly see that the decay of device with 300 °C TiO2 Cl is much faster than that in the 400 °C device, which is a strong support to the aforementioned free carrier behaviour results.

To check whether the obtained results of these CH3NH3PbI3 devices works for its FA0.81MA0.15Pb(I0.836Br0.15)3 counterpart, we have fabricated some FA0.81MA0.15Pb(I0.836Br0.15)3 devices based on these TiO2 compact layers. The same efficiency distribution can be observed among these devices. As can be seen from Fig. 7 and Table 2, the standard device fabricated with 400 °C TiO2 compact layer shows the highest efficiency of 16.6% with a 1.06 V of Voc, 22.87 mA cm-2 of Jsc and a FF of 0.68. However, the average device with 300 °C TiO2 compact layer exhibits Jsc of 11.5 mA cm-2, Voc of 1.02 V, FF of 0.56 and overall PCE of 6.8%, which is much smaller than that of 400 and 500 °C samples. The device performance of other compact layer annealing temperatures can be found in Table S2.

According to recent publications, high density of oxygen vacancies also showed negative impact on the stability of the perovskite sensitized TiO2 solar cell [9,32,33]. So the methods for fabricating high efficiency and stable TiO2 based PSC are summarized as: controlling the annealing temperature and time properly in order to get relatively high quality TiO2 with appropriate levels of oxygen vacancies and crystallinity, the immediate use of heated TiO2 sample for device fabrication in order to prevent wastes

Table 2
Photovoltaic parameters derived from J-V measurements of CH3NH3PbI3 and FA0.81MA0.15Pb(I0.836Br0.15)3 based champion device with different TiO2 CLs.

<table>
<thead>
<tr>
<th>TiO2 Annealing temperature (°C)</th>
<th>Voc (V)</th>
<th>Jsc (mA/cm2)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 CH3NH3PbI3</td>
<td>0.91</td>
<td>9.80</td>
<td>0.47</td>
<td>4.2</td>
</tr>
<tr>
<td>FA0.81MA0.15PbI0.836Br0.15I3</td>
<td>1.02</td>
<td>11.50</td>
<td>0.56</td>
<td>6.8</td>
</tr>
<tr>
<td>400 CH3NH3PbI3</td>
<td>0.99</td>
<td>22.00</td>
<td>0.68</td>
<td>14.9</td>
</tr>
<tr>
<td>FA0.81MA0.15PbI0.836Br0.15I3</td>
<td>1.06</td>
<td>22.87</td>
<td>0.68</td>
<td>16.6</td>
</tr>
<tr>
<td>500 CH3NH3PbI3</td>
<td>1.01</td>
<td>21.00</td>
<td>0.67</td>
<td>14.3</td>
</tr>
<tr>
<td>FA0.81MA0.15PbI0.836Br0.15I3</td>
<td>1.06</td>
<td>21.25</td>
<td>0.68</td>
<td>15.5</td>
</tr>
</tbody>
</table>

Fig. 5. (a) Current–voltage characteristics of the champion PSCs with different TiO2 CLs measured under dark and simulated 1 sun condition. (b) The corresponding IPCE spectra of these samples. (c–e) Schematic diagrams of free electron transport through 300 °C TiO2/CH3NH3PbI3, 400 °C TiO2/CH3NH3PbI3 and 500 °C TiO2/CH3NH3PbI3 interfaces, the red e- represent the accumulated carriers at the interface and the blue arrows show the free electrons trapped by organic residues and oxygen vacancies. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).
adsorption at the surface and correctly tuning the interface potential barrier and reduce the oxygen vacancies by interface engineering methods such as metal-loading, impurity doping, inorganic adsorbates, polymer coating, dye-sensitization, charge transfer complexation [34].

4. Conclusions

In conclusion, we have investigated the atomic, electronic structures and charge carrier transporting mechanisms at the CH$_3$NH$_3$PbI$_3$/TiO$_2$ interface. The evidence of potential interfacial barrier was observed at the CH$_3$NH$_3$PbI$_3$/TiO$_2$ interfaces. The performance of different planar PSCs exhibited close correlation between solar cell efficiency and surface properties of TiO$_2$, such as oxygen vacancies, organic residues and crystallinity. In addition, we have elaborated the photogenerated carrier transport processes through different CH$_3$NH$_3$PbI$_3$/TiO$_2$ heterojunctions. Our work indicates that efficient charge carrier transport at the interface and ideal PSCs with theoretical efficiency can be developed by correctly tuning the TiO$_2$ layers.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.solmat.2017.01.005.

References


