Boosting efficiency of planar heterojunction perovskite solar cells by a low temperature TiCl_4 treatment

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It is well known that electron transport layer (ETL) plays an indispensable role in the planar heterojunction perovskite solar cells (PSCs). TiO_2 is widely used as an ETL material due to its excellent transport properties, however, the presence of defects in the TiO_2 layer diminishes the power conversion efficiency (PCE) of the devices. Herein, we introduce a method of low-temperature TiCl_4 treatment to deposit a TiO_x layer on the surface of TiO_2 film, which can effectively passivate trap states at the TiO_2 surface. Moreover, the treating process is optimized to be 30 min using a 40 mM TiCl_4 aqueous solution. Benefiting from this, we obtain the champion device with the highest PCE of 18.47%, which is mainly due to the reduction of surface defects and the deposition of the well-crystallized perovskite films. Besides, the modified PSCs exhibit an average PCE of 17.59%, which is much better than the control devices.

Keywords: Perovskite solar cells; TiO_2 ; TiCl_4 ; surface modification.

1. Introduction

Over the past years, the organic–inorganic hybrid perovskite solar cells (PSCs) have attracted particular attention owing to their excellent charge transport properties,¹ large absorption coefficient² and broad absorption band.³ Benefit from these excellent properties, the power conversion efficiency of PSCs has rapidly increased from 3.8% in 2009⁴ to 22.7% in 2017.⁵ At present, the two main structures in the field of perovskite solar cells are mesoscopic structure⁶ and planar heterojunction structure.⁷ The most prominent characteristic of the mesoscopic structure is the introduction of nanoparticles as a mesoporous scaffold, so that the perovskite precursor solution filled inside the scaffold adequately to obtain a continuous and uniform perovskite film. At the same time, due to the simple device structure and fabrication process, the planar heterojunctions PSCs have achieved rapid development as well. In this structure, the perovskite active layer is sandwiched between charge selective transport layers^{8,9} without the mesoporous scaffold, thereby making the PSCs preparation more simplified and reducing the constraint of the device preparation conditions.

In the planar heterojunction structure, the electron transport layer (ETL) between the active perovskite material and the cathode plays a significant role in hole blocking and electron extraction. Currently, the materials used for the ETL includes organic materials and inorganic materials such as TiO_2 ,¹⁰ ZnO ,^{11,12} SnO_2 ¹³ and phenyl-C61-butyric acid methyl ester (PCBM), etc.¹⁴ Among them, TiO_2 is the most widely used ETL material, mainly owing to its chemical stability,¹⁵ electronic and optical properties¹⁶ and compatibility with various deposition methods.¹⁷ Nevertheless, there are numerous trap states in the surface of TiO_2 films, leading to ineffective charge transportation and severe charge recombination.¹⁸ As an effective method to modify the surface of TiO_2 films, chemical bath deposited TiO_x films have been proposed by some researchers to improve the performance of the PSCs. For example, Yella *et al.* introduced a low-temperature route for the fabrication of $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$ solar cells using TiCl_4 chemical bath deposition technique and thus achieved better performance.¹⁹ In addition, Liu *et al.* confirmed TiCl_4 treatment improved the contact of the TiO_2 /perovskite interface, facilitating charge extraction and

suppressing charge recombination.²⁰ Similarly, Murakami *et al.* also studied the mechanism of TiCl_4 treatment and demonstrated that through the TiCl_4 treatment, the conduction band edge of the compact TiO_2 layer was shifted to a higher level and the performance of PSC was improved.²¹ However, the relationship between the performance of device and the TiCl_4 treating time remains unclear.

Herein, we employed a facile TiCl_4 treatment method with certain concentration to improve the surface properties of TiO_2 and systematically studied the effect of treating time on the performance of the devices. We optimized the treatment time as 30 min and obtained a more uniform and less pinhole ETL after treatment. As a result, the devices based on the structure of FTO/ TiO_x /perovskite (PVSK)/spiro-OMeTAD/Ag showed dramatic improvement of FF and J_{SC} , leading to the champion efficiency of 18.47% with an average value of 17.59%, which was much better than the control devices.

2. Experimental Section

2.1. Materials and chemicals

Li-bis-(trifluoromethanesulfonyl) imide (Li-TFSI), 4-tert-butylpyridine (TBP), dimethylsulphoxide (DMSO), chlorobenzene (CB) and N, N-dimethylformamide (DMF) were supplied by Alfa-Aesar. $\text{CH}_3\text{NH}_3\text{I}$ (MAI, 95%), lead iodide (PbI_2 , 99.9%) and 2,2',7,7'-tetrakis (N, N-di-p-methoxyphenylamine)-9,90-spirobifluorene (spiro-OMeTAD, 99.5%) were purchased from Xi'an p-OLED. Other reagents including TiCl_4 (Chemically Pure) were received from Sinopharm Chemical Reagent.

2.2. Substrate Preparation and surface treatment

FTO-coated glass sheets were patterned by a selective etching with diluted HCl aqueous solution and Zn powders, then cleaned sequentially by ultrasonication in Hellmanex detergent diluted in deionized (DI) water, DI water, acetone and ethanol for 15 min each. After that, a UV-ozone treatment was performed for 15 min.

2.3. Solar cell fabrication

The compact TiO_2 layer was obtained by spin-coating a solution prepared by mixing 10 ml of ethanol, 109 mg of diethanolamine and 471 mg of tetrabutyl titanate at 500 rpm for 6 s and 3000 rpm for 30 s.²² Then, the film was annealed at 500°C for 30 min. After cooling to room temperature, the substrates were treated by a UV-Ozone for 15 min again. The substrates with TiO_2 films were then immersed in 40 mM aqueous TiCl_4 solution at 70°C for various time. Following, the samples cleaned by ethanol and dried with clean N_2 . And then all the samples were annealed at 130°C for 30 min together. After that, the perovskite solution was deposited in a one-step process by spin-coating at 1000 rpm for 5 s and then

at 3000 rpm for 30 s. During the second spin-coating step, 130 μl CB was dropwise added onto the wet film. Here, the perovskite precursor solution was prepared by dissolving of 1 mmol PbI_2 and 1 mmol $\text{CH}_3\text{CH}_2\text{I}$ with different molar ratios in 1 ml mixed solvents of DMSO: DMF = 3:7. The mixture was stirred at 70°C for more than 6 h and filtered through a PTFE filter (0.45 μm) before use. Thereafter, the perovskite film was annealed at 70°C for 4 min and then annealed at 100°C for 20 min. Then a hole-transport layer precursor solution was prepared by dissolved Spiro-OMeTAD (72.3 mg), 4-tert-butylpyridine (28.8 μl) and Li-TFSI/acetonitrile (17.5 μl , Aldrich) in CB (1 ml). The final solution was stirred for one night and then spin-coated onto the perovskite films as the hole-transporting layer at a speed of 2000 rpm for 30 s. Finally, the monolithic device fabrication was completed by evaporating the Ag back electrode.

2.4. Characterization

The crystallinity of the samples was characterized by X-ray diffraction (XRD, D/max 2400 X Series, Rigaku, Japan). Energy dispersive spectrum (EDS) mapping of the 30 min TiCl_4 treatment on the TiO_2 films were observed using a field emission SEM (FE-SEM, Quanta F250, JEOL Inc., Japan). The absorption and transmittance spectra of the films were tested by a JASCOV-570 UV/VIS/NIR spectrometer. The current density–voltage (J – V) characteristics under AM 1.5G simulated solar illumination were measured using a PVIV-201V I–V Station (Newport Oriel), and the prepared devices were reversely scanned (1.2 V $\rightarrow$ –0.1 V, 66 data points) with a 100 ms time interval.

3. Results and Discussion

To elucidate the changes of morphologies after TiCl_4 treatment, we treated the FTO/ TiO_2 substrates with a certain concentration of TiCl_4 aqueous solution with different times to deposit a TiO_x layer. For the sake of simplicity, the samples will be labeled TiCl_x , where x denotes the TiCl_4 treating time, e.g., TiCl_{30} corresponds to a FTO/ TiO_2 sample with 30 min TiCl_4 treatment. Firstly, the samples were carried out with SEM characterization as shown in Fig. 1. In Fig. 1(a), it can be seen that there are some cracks on the surface of the untreated films, which may be attributed to the incomplete coverage of the substrates with TiO_2 films fabricated at high temperature. The presence of these surface cracks may lead to direct contact of the perovskite films with the substrates, thereby decreasing the PCE of devices. As shown in Figs. 1(b)–1(d), after the TiCl_4 treatment, a large proportion of cracks are eliminated. The improvements of these surface morphologies are due to fact that the post-treatment deposited TiO_x on the surface of TiO_2 fills these cracks and makes the surface smoother. Therefore, it is found that the TiCl_4 treatment did improve the morphology of TiO_2 films. To explore the elemental distribution of TiCl_4 -treated films, we

Fig. 1. Top-view SEM images of FTO/TiO₂ substrates with different TiCl₄ treating time: (a) TiCl₀, (b) TiCl₁₅, (c) TiCl₃₀ and (d) TiCl₆₀. EDS images (e) Cl element, (f) Ti element and (g) O element mapping showing the effect on 30 min TiCl₄ treatment of FTO substrates.

conducted EDS mapping measurement. Figures 1(e)–1(g) shows the Cl element, Ti element and O element, respectively. It can be seen that although the thermal treatment at 130°C has been carried out after TiCl₄ treatment, Cl elements still preserved, and these three elements are uniformly distributed on the surface of the films. Other researchers demonstrated that Cl ions affect the growth of the CH₃NH₃PbI₃ and the presence of Cl ions source in the starting solutions used for the perovskite deposition resulted in a strong increase of the overall charge diffusion length.^{23,24} Therefore, it can be speculated that the presence of the Cl ions on the surface of the films can improve the device performance.

To gain insight into the influence of TiCl₄ treatment on the optical properties of TiO₂, we performed a transmittance measurement. As depicted in Fig. 2, after treated with TiCl₄, the transmittances of TiO₂ substrates were slightly lower than the control sample. Moreover, there is no significant difference in the transmittances of TiO₂ substrates as for different treating time, indicating that the treating time has little effect on the transmittances over a wide time range.

The quality of perovskite films directly affects the device performance of PSCs. Therefore, to investigate the effect of post-treatment of TiO₂ on the deposition of the perovskite film, we deposited perovskite thin films on top of the TiO₂ films with 30 min TiCl₄ treatment. The analysis of absorption spectra, XRD and SEM have been investigated. Figure 3(a) shows the spectra of absorption for the planar heterojunction PSCs with and without TiCl₄ treatment. It can be found that

Fig. 2. Transmission spectra of TiO_x deposited on TiO₂-coated FTO with different TiCl₄ treating time (0, 15, 30 and 60).

the absorbance was enhanced for perovskite films on 30 min TiCl₄ treated TiO₂ as compared with the control samples. To study the effect of TiCl₄ treatment on the crystallization of perovskites, XRD characterization was performed as shown in Fig. 3(b). The two curves show the same characteristic peaks at 14.2°, 28.5° and 31.8°, which are indexed to the (110), (220) and (310) planes of the CH₃NH₃PbI₃. Meanwhile, the XRD patterns show that the crystallinity of the

Fig. 3. (a) Absorption spectra of perovskite films deposited on the TiO₂ films with 30 min or without TiCl₄ treatment. (b) XRD patterns of perovskite films on the TiO₂ films with 30 min or without TiCl₄ treatment. (c) Top-view SEM images of perovskite films on TiO_x films.

perovskite films is not affected by the post-treatment. Then, we further observed the morphology of the perovskite films deposited on TiCl₄-treated TiO₂ surface by SEM as shown in Fig. 3(c). It is found that perovskite films exhibit smooth, uniform and large crystal grains on the TiO_x films.

Based the above studies, it can be found that TiCl₄ treatment can improve the surface morphology of TiO₂ films and has an insignificant effect on the crystallinity of the perovskite films. To further determine the optimal treating time,

we have assembled the resulting planar heterojunction PSCs. These devices employ TiO₂ and Spiro-OMeTAD as the charge extraction layer, with the active layer of perovskite sandwiched between them and an Ag electrode as the back electrode. Unlike other devices using TiO₂ as ETL, we deposited a TiO_x film by TiCl₄ treatment of different time on the surface of TiO₂ before the perovskite deposition as shown schematically in Fig. 4(a). In addition, the cross-sectional SEM based on the TiO_x/TiO₂ ETL is shown in Fig. 4(b).

Fig. 4. (a) Schematic illustration of the device structure. (b) The cross-sectional SEM micrograph of typical PSC devices.

Fig. 5. The box-chart images of (a) open-circuit voltage (V_{OC}), (b) short-circuit current density (J_{SC}), (c) fill factor (FF) and (d) power conversion efficiency (PCE) for devices with different $TiCl_4$ treating time (0, 15, 30 and 60) which extracted from measuring current density-voltage curves at simulated one sun illumination.

The values of the device parameters, such as open-circuit voltage (V_{OC}), short-circuits current density (J_{SC}), fill factor (FF) and PCE are shown in Fig. 5 with box-charts. These photovoltaic properties were evaluated under standard simulated sunlight (AM 1.5G) irradiation at a reverse scan. The mean values and standard deviations of the photovoltaic performance parameters are listed and compared in Table 1. It can be found that, as the time of the $TiCl_4$ treatment increases from 0 to 30 min, the V_{OC} remains nearly constant around 1.10 V and the average J_{SC} increases from 20.68 to 22.20 mA/cm^2 . This enhancement of J_{SC} is consistent with an increase of absorption shown after the surface treatment of the perovskite films in Fig. 3(a). As reported before, several mechanisms should be accounted for the increase of J_{SC} . Firstly, a shift in the conduction band edge of the TiO_2 after $TiCl_4$ treatment improves the capacity of charge injection into the TiO_2 .²⁵ Secondly, the $TiCl_4$ post-treatment passivates the defect sites of TiO_2 and reduces the rate of recombination.²⁶ Thirdly, the $TiCl_4$ treatment enhances transport in the active layer, which supports lower recombination and enhances charge collection at the adjacent contact.²⁷ Moreover, the average fill factor (FF) obtained with three different treatment

($TiCl_0$, $TiCl_{15}$, $TiCl_{30}$) are $65.11 \pm 1.2\%$, $69.22 \pm 1.3\%$ and $72.14 \pm 2.3\%$, respectively. In general, smaller series resistance (R_s) and larger shunt resistance (R_{sh}) will get larger FF. Here, the increase in FF is mainly due to better contact between perovskite film and TiO_2 film, higher perovskite film coverage, and better hole-blocking abilities after $TiCl_4$ treatment, which resulting in the decreasing of R_s and the increasing of R_{sh} .^{20,28} The average PCE of devices without treatment is $14.70 \pm 0.4\%$ and increase to $16.46 \pm 0.5\%$ and $17.59 \pm 0.6\%$ after surface treatment of the $TiCl_4$ for 15 and 30 min. This further confirms that the performance of $TiCl_4$ -treated cells is much better than that of control devices with a

Table 1. Average photovoltaic parameters for PSCs devices extracted from J-V curves in Fig. 5.

Samples	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
$TiCl_0$	1.09 ± 0.006	20.68 ± 0.4	65.11 ± 1.2	14.70 ± 0.4
$TiCl_{15}$	1.10 ± 0.003	21.57 ± 0.4	69.22 ± 1.3	16.46 ± 0.5
$TiCl_{30}$	1.10 ± 0.007	22.20 ± 0.1	72.14 ± 2.3	17.59 ± 0.6
$TiCl_{60}$	1.09 ± 0.004	21.59 ± 0.4	67.85 ± 2.1	16.11 ± 0.4

Fig. 6. The J-V curves and photovoltaic parameters measured from the devices with the structure of FTO/ TiO_2 / $TiCl_{30}$ /PVSK/spiro-OMeTAD/Ag.

bare TiO₂ ETL. However, when we continued to increase the treating time, the J_{SC} , FF and PCE decreased to $21.59 \pm 0.4 \text{ mA/cm}^2$, $67.85 \pm 2.1\%$ and $16.11 \pm 0.4\%$, respectively. It is likely to be attributed to that, as the treating time increases, the thickness of TiO_x films and resistance increase, which results in the decrease of PCE. Therefore, we optimized the treating time to be 30 min. In the end, we showed the J–V curves and photovoltaic parameters of the optimal PSCs based on 30 min TiCl₄ treatment in Fig. 6. Benefit from the modification of the surface of ETL with the optimal treating time, the champion PCE of 18.47% is achieved, with V_{OC} , J_{SC} , and FF of 1.086 V, 2.20 mA/cm² and 72.14%, respectively. This series of values indicate that TiCl₄ treatment is an effective method to improve the performance of device.

4. Conclusion

In summary, we employed a surface modification method of low-temperature TiCl₄ treatment, depositing a TiO_x layer on the surface of TiO₂ films for planar heterojunction perovskite solar cells (PSCs). The treatment was optimized to be 30 min using a 40 mM TiCl₄ aqueous solution. We found that the insertion of TiO_x can significantly reduce the defects and effectively improve the smoothness of TiO₂ surface. As a result, the devices with the structure of FTO/TiO₂/TiO_x/PVSK/spiro-OMeTAD/Ag showed a dramatic enhanced average PCE from 14.70% to 17.59% with the maximum PCE of 18.47%. Our research results demonstrate that the surface modification method of low-temperature TiCl₄ treatment with appropriate treating time could be an effective way to obtain highly efficient PSCs.

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