Enhanced performance of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ perovskite solar cells by CH$_3$NH$_3$I modification of TiO$_2$-perovskite layer interface

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Abstract

In this work, perovskite solar cells (PSCs) with CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ as active layer and spiro-OMeTAD as hole-transport media have been fabricated by one-step method. The methylammonium iodide (CH$_3$NH$_3$I) solution with different concentrations is used to modify the interface between mesoporous TiO$_2$ (meso-TiO$_2$) film and CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ perovskite layer. Several techniques including X-ray diffraction, scanning electron microscopy, optical absorption, electrochemical impedance spectroscopy (EIS) and photoluminescence are used to investigate the effect of the interfacial modification. It is found that the interfacial modification by CH$_3$NH$_3$I enhance the crystallinity and increase the grain size of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ layer, and improve the surface wetting properties of perovskite precursor on meso-TiO$_2$ film. The sunlight absorption and external quantum efficiency of PSCs in the visible region with wavelength less than 600 nm have been improved. The Nyquist plots obtained from the EIS suggest that the CH$_3$NH$_3$I modification can reduce the charge recombination rates. The photoluminescence measurement shows that the exciton dissociation in the modified devices is more effective than that in the control samples. The photovoltaic performance of the modified devices can be significantly improved with respect to the reference (control) devices. The CH$_3$NH$_3$I modified devices at the optimized concentration demonstrate the average power conversion efficiency of 12.27 % in comparison with the average efficiency of 9.68 % for the reference devices.

Keywords: CH$_3$NH$_3$I, Interfacial modification, CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ perovskite solar cells, Photoelectronic properties, Performance

Background

Recently, solar cells based on composites of organometallic halide perovskite have attracted much attention due to their super high absorption coefficients, relatively high carrier mobility and easy fabrication by solution process [1–3]. The efficiency of perovskite (CH$_3$NH$_3$PbX$_3$, $X$ = Cl, Br, I)-based photovoltaic devices has greatly increased from 3.8 % to more than 20 % in just a few years [4–6]. It is well known that the microstructure and crystallinity of perovskite layer have important influence on the performance of perovskite solar cells (PSCs) [7]. The morphology of the perovskite films influences on exciton separation, charge transfer, and recombination [8]. The low crystallinity of the perovskite films will result in a strong leakage path and has a negative effect on the charge dynamics of PSCs [5, 9]. However, a precise control of the morphology and crystallinity of perovskite layer remains a critical challenge due to the complex crystal growth mechanism of the perovskite materials. Substantial effort has been done to improve the microstructure of PSCs by adjusting the perovskite crystallization kinetics, such as additives modification [10], composition optimization [11], solvent extraction [12], and controlling the temperature, annealing time, or atmosphere [13–15]. However, a control of the crystalline property and
microstructure just by optimizing the fabrication processing seems to be insufficient.

It is known that surface modification has been widely used to improve the performance of organic solar cells and dye-sensitized solar cells [16–19]. Interfacial engineering has been also used as a new strategy to control the morphology of perovskite layer and improve the efficiency of PSCs. It is found that interfacial modification can significantly promote the charge transfer and reduce the recombination rate for those PSCs with metal oxides as electron transport materials [20–22]. It was reported that a modification of the interface between ZnO and perovskite layer using self-assembled monolayer can optimize the morphology of perovskite layer and improve the performance of PSCs [23, 24]. It was also demonstrated that modifying the TiO$_2$/CH$_3$NH$_3$PbI$_3$ heterojunction interface by glycine can enhance the photovoltaic performance of two-step solution-processed PSCs [25].

In addition, a modification of the perovskite/TiO$_2$ interface with a nanoscale layer of Al$_2$O$_3$ can reduce the charge losses of the PSCs [26]. Excess CH$_3$NH$_3^+$ or methylammonium iodide (CH$_3$NH$_3$I) is very important for the improvement in the optoelectronic properties of perovskite layer. Better coverage, uniform and pinhole-free perovskite films by adding excess CH$_3$NH$_3^+$ to the reactants of perovskite layer can be obtained [27]. During the preparation of perovskite layer by sequential deposition method, a proper addition of CH$_3$NH$_3$I to PbI$_2$ solution not only enhances the absorption but also reduces the recombination rate, resulting in the improvement of efficiency in PSCs [28]. These results suggest that it is possible to introduce CH$_3$NH$_3$I to modify the interface of PSCs.

Based on these considerations, in this work, the PSCs with the glass/FTO/compact TiO$_2$/meso-TiO$_2$/CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$/spiro-OMeTAD/Ag structure are fabricated by the one-step solution method. Here, we choose CH$_3$NH$_3$I to modify the interface between meso-TiO$_2$ and CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ perovskite layer and investigate the effect of CH$_3$NH$_3$I concentration on the microstructure of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ layer and photovoltaic properties of the PSCs. The related mechanism is addressed too. The results show that the CH$_3$NH$_3$I modification at the optimal concentration can improve the sunlight absorption and external quantum efficiency (EQE) in the visible region at the wavelengths less than 600 nm, reduce the charge recombination rate, and promote the charge transfer, resulting in the enhanced performance. The average power conversion efficiency (PCE) of the PSCs can be enhanced from 9.68 to 12.27 %, respectively.

**Methods**

Figure 1 shows a schematic diagram of the PSCs fabricated in this work. First, each pre-cleaned FTO substrate was coated with a 60-nm TiO$_2$ blocking film by spinning a sol-gel solution (0.25 M titanium isopropoxide in ethanol) at 4000 rpm. The layer was annealed at 500 °C for 30 min to allow sufficient crystallization in ambient air. The meso-TiO$_2$ layer was deposited on the TiO$_2$ blocking film by spin-coating a TiO$_2$ solution (18NR-T, Dyesol) in ethanol at 6000 rpm. These samples were then sintered at 550 °C for 30 min in air to obtain meso-TiO$_2$ films. For every batch, several of the as-prepared samples were chosen as the reference samples and the other samples were submitted to next processing.

CH$_3$NH$_3$I was synthesized using the reported method [3]. For the CH$_3$NH$_3$I modification, the CH$_3$NH$_3$I of different concentration dissolved in isopropanol was spin-coated on the meso-TiO$_2$ films at 4000 rpm. The untreated samples were chosen as the references. After the modification, these samples together with the reference samples were annealed at 60 °C for 30 min. CH$_3$NH$_3$I and PbCl$_2$ (Aladdin, 99.5 %) were dissolved in N,N-dimethylformamide (Aladdin, 99.9 %) to obtain a 40 wt % precursor solution with a CH$_3$NH$_3$I:PbCl$_2$ molar ratio of 3:1. The solution was filtered with a 0.45-µm pore size filters before spin-coating. To fabricate the PSCs from the above samples, a CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ layer was deposited onto the meso-TiO$_2$ film by spin-coating a solution of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ (40 wt % dissolved in DMF) at 2000 rpm for 30 s in the glove box. Then, these samples were annealed in nitrogen (N$_2$) ambient at 100 °C for 45 min. Subsequently, 0.08 M spiro-OMeTAD in chlorobenzene solution was spin-coated onto the perovskite film. These samples were left in dry air overnight in the dark. Finally, Ag electrodes with thickness of ~100 nm were evaporated on the sample surface through a shadow mask under a vacuum of 1 × 10$^{-4}$ Pa. All the as-prepared PSCs were fabricated with the standard in-plane size of 3 mm × 4 mm.

**Device Characterizations**

The morphology and crystallinity of the perovskite layer were investigated using scanning electron microscopy (SEM, ZEISS ULTRA 55) and the X-ray diffraction (XRD) (X’Pert PRO, Cu Kα radiation). The photovoltaic
performance of these PSCs was characterized using a Keithley 2400 source meter under an illumination of 100 mW/cm² (Newport 91160, 150 W solar simulator equipped with an AM 1.5 G filter). The radiation intensity was calibrated by a standard silicon solar cell (certified by NREL) as the reference. The EQE and the UV-vis absorption spectra were measured using an AM 1.5 G filter. The electrochemical impedance spectroscopy (EIS) measurements were performed on the Zahner Zennium electrochemical workstation in the dark. A 20-mV ac-sinusoidal signal source was employed over the constant bias with the frequency ranging from 1 Hz to 4 MHz. The photoluminescence spectra (PL) were measured by a fluorescence spectrophotometer (HITACHI F-5000) excited at 405 nm. The PL spectra have been normalized to the absorbance and measured in the same conditions.

**Results and Discussion**

It is known that the interfacial property has a significant influence on the photovoltaic properties of the PSCs. In this work, it is found that the performance of CH₃NH₃PbI₃−ₓClₓ PSCs are influenced remarkably by the concentration of CH₃NH₃I solution used to modify the interface between the meso-TiO₂ and CH₃NH₃PbI₃−ₓClₓ. To investigate the effect of CH₃NH₃I on the performance of PSCs, CH₃NH₃I solutions of different concentration at 0, 5, 10, and 20 mg/ml were used, labeled as x (x = 0, 5, 10, 20). Initially, we investigated the effect of CH₃NH₃I modification on the crystalline structure of CH₃NH₃PbI₃−ₓClₓ perovskite materials. Figure 2a shows the XRD patterns of CH₃NH₃PbI₃−ₓClₓ layers deposited on the meso-TiO₂ film without and with modification by CH₃NH₃I solutions with different concentrations. The peaks at 14.10°, 28.47°, 43.27°, and 58.88° can be attributed to the (110), (220), (330), and (440) reflections of the perovskite crystalline structure, respectively [23]. The presence of these peaks indicates the successful conversion into the perovskite structure, similar to earlier reports [27, 29]. The intensity of all these perovskite diffraction peaks enhances after the CH₃NH₃I modification and attains the maximum at x = 10. Figure 2b shows the detailed information of the XRD patterns from 13° to 15°. It can be seen that the intensity of (110) characteristic peak increases with the concentration of CH₃NH₃I and attains the maximum at x = 10 and then decreases with the increase of CH₃NH₃I concentration. This implies that the crystallinity of CH₃NH₃PbI₃−ₓClₓ film increases upon the CH₃NH₃I modification [8]. The improved crystallinity and preferred growth in the (110) direction can be attributed to the excess of CH₃NH₃⁺ which slows the crystallization rate of perovskite layer [27, 28].

The interfacial modification of CH₃NH₃I also plays a critical role in the morphology of perovskite layer. The top-view SEM images of CH₃NH₃PbI₃−ₓClₓ films deposited on meso-TiO₂ modified by CH₃NH₃I solutions with different concentrations are presented in Fig. 3. It can be seen that the pinholes decrease and the grain size of CH₃NH₃PbI₃−ₓClₓ increases upon the CH₃NH₃I modification, which will benefit to the performance improvement [9]. For high efficiency PSCs, pinhole-free perovskite films with high crystalline properties are very important. In this view, the enhanced crystalline property and morphology evolution after CH₃NH₃I modification may promise an improved device performance of PSCs, which will be discussed below. Figure 4 shows the contact angles of CH₃NH₃PbI₃−ₓClₓ precursor solution directly dropped on meso-TiO₂ with and without CH₃NH₃I modification. As seen in Fig. 4, the contact angle decreases with increasing CH₃NH₃I concentration.

![Fig. 2](image-url) (Color online) a X-ray diffraction (XRD) patterns of CH₃NH₃PbI₃−ₓClₓ perovskite layer. b Detail XRD information of CH₃NH₃PbI₃−ₓClₓ from 13° to 15°. The perovskite was deposited on meso-TiO₂ modified by CH₃NH₃I solutions with different concentrations.
concentration. It implies that the surface wetting properties of perovskite precursor on meso-TiO$_2$ film are improved after the CH$_3$NH$_3$I modification, which will facilitate to improve the coverage rates of perovskite layer [30].

To investigate the effect of CH$_3$NH$_3$I modification on the performance of PSCs, the devices based on the structure illustrated in Fig. 1 are fabricated. Figure 5 shows the detailed photovoltaic parameters including the open-circuit voltage ($V_{oc}$), the short-circuit current density ($J_{sc}$), fill factors (FF), and PCE for the devices with different CH$_3$NH$_3$I concentrations. The photovoltaic parameters for those devices are summarized in Table 1. The device without CH$_3$NH$_3$I modification exhibits an average PCE of 9.68 % and the best PCE of 10.55 %. After the modification by CH$_3$NH$_3$I solution at $x = 10$, the best PCE of PSCs reaches 12.44 %. The device exhibits $J_{sc} \approx 20.41$ mA/cm$^2$, $V_{oc} \approx 884$ mV, and FF $\approx 68.01$, yielding an average PCE of 12.27 %. The CH$_3$NH$_3$I modification improves all the device parameters at the optimal concentration of 10 mg/ml. When the concentration of CH$_3$NH$_3$I is increased to 20 mg/ml, $V_{oc}$ and FF decrease, leading to lower PCE. This can be attributed to too much excessive CH$_3$NH$_3$I caused by the higher concentration, resulting in a redundant impurity to hinder charge transport [27].

Figure 6a presents the $J$-$V$ curves of PSCs without and with CH$_3$NH$_3$I modification at $x = 10$. Remarkably, the average PCE increases to 12.27 % after CH$_3$NH$_3$I modification. The introduction of the CH$_3$NH$_3$I results in significantly enhancement of PCE. The $J_{sc}$ increases from 19.44 to 20.41 mA/cm$^2$, $V_{oc}$ from 826 to 884 mV, FF from 60.3 to 68.0 %, and the average PCE from 9.68 to 12.27 % for the reference device and modified device at the optimal concentration, respectively. For PSCs, the device performance variation is usually observed from batch to batch. In this work, we have fabricated 28 devices for 7 batches.
to confirm the effect of CH$_3$NH$_3$I modification on the performance. Figure 6b shows the statistic histogram of PCE for the device without and with the CH$_3$NH$_3$I modification at different concentrations. The device performance of PSCs with CH$_3$NH$_3$I modification at the optimal concentration exhibits a narrowed distribution of PCE (range, 11.45 to 12.44 %, with the averaged value of 12.27 %). However, the reference devices show much lower PCE (averaged value 9.68 %) in a wide range (from 8.80 to 10.55 %). Obviously, the improved performance and better reproducibility verified the significance of CH$_3$NH$_3$I interfacial modification. The possible mechanisms for the enhanced performance of PSCs will be explored below. To further investigate the origin of the increase of $J_{sc}$, the absorption spectra and EQE curves for the reference device and modified device by CH$_3$NH$_3$I solution at the optimal concentration of 10 mg/ml are presented in Fig. 7, respectively. As shown in Fig. 7, the CH$_3$NH$_3$I modification obviously increases the light absorption and EQE in the visible region at the wavelengths less than 600 nm. The enhanced absorbance and EQE contribute to the improvement of $J_{sc}$ in the modified device.

In order to get a better understanding of the microscopic mechanisms for the observed enhancement of the performance upon the CH$_3$NH$_3$I modification, the EIS is carried out to characterize the charge transfer dynamics of PSCs. The Nyquist plots for PSCs measured at -0.8 V (close to $V_{oc}$) in the dark are presented in Fig. 8a. The solid lines in Fig. 8a are the fits of experimental data using the model in the panel of Fig. 8b. For more accurate fitting, the CPE is used instead of the ideal capacitance $C$ to account for spatial inhomogeneities induced by defects and impurities at the interface. It is can be seen that the measured Nyquist plots can be fitted well by the panel in Fig. 8b. The Nyquist plots consist of two semicircles (See Additional file 1: Figure S1). The first arc at higher frequencies is related to the charge transport and extraction in the Au electrode [30]. The main semicircle is related to the charge recombination at TiO$_2$/CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$/spiro-OMeTAD interface. Similar results have also been reported in the literature [25, 31–34]. The significant difference can be seen in the Nyquist plots of the PSCs with and without CH$_3$NH$_3$I modification. The size of the arc increases with the increase of the concentration of CH$_3$NH$_3$I solution and then decreases when the concentration increases to 20 mg/ml, as shown in Fig. 8a. Figure 8c shows the fitted values of the recombination resistance ($R_{rec}$) for PSCs without and with CH$_3$NH$_3$I modification of various concentrations at different bias voltages. It is noted that the device with CH$_3$NH$_3$I

### Table 1 The photovoltaic parameters of the PSCs modified by CH$_3$NH$_3$I with different concentrations

| CH$_3$NH$_3$I (mg/ml) | $V_{oc}$ (mV) | $J_{sc}$ (mA/cm$^2$) | FF (%) | PCE (%) | Average | Best |
|------------------------|---------------|----------------------|--------|---------|---------|------|
| 0                      | 826           | 19.44                | 60.27  | 9.68    | 10.55   |      |
| 5                      | 842           | 19.11                | 64.90  | 10.44   | 11.21   |      |
| 10                     | 884           | 20.41                | 68.01  | 12.27   | 12.44   |      |
| 20                     | 883           | 19.43                | 67.56  | 11.59   | 11.97   |      |
modification exhibits the higher \( R_{\text{rec}} \) than the device without \( \text{CH}_3\text{NH}_3\text{I} \) modification. It indicates that the recombination rate decreases after the \( \text{CH}_3\text{NH}_3\text{I} \) modification because the recombination rate is inversely proportional to \( R_{\text{rec}} \) [35]. This will benefit for the charge transfer from perovskite to TiO\(_2\) [25]. Because all devices are fabricated at the same process except for the \( \text{CH}_3\text{NH}_3\text{I} \) modification, the difference in recombination rate can be attributed to the interface modification of \( \text{CH}_3\text{NH}_3\text{I} \). The device modified by \( \text{CH}_3\text{NH}_3\text{I} \) solution at \( x = 10 \) shows the largest \( R_{\text{rec}} \) at the same bias voltage, corresponding to the lowest recombination rate. This result is consistent with the variation tendency of the \( V_{\text{oc}} \) as a function of \( \text{CH}_3\text{NH}_3\text{I} \) concentrations. It is notable that \( V_{\text{oc}} \) is strongly influenced by the recombination rate at the heterojunction of a solar cell [36, 37]. Lower recombination rate in solar cells will lead to a higher \( V_{\text{oc}} \).

Therefore, the significant improvements of the \( V_{\text{oc}} \) and the PCE of the PSCs after \( \text{CH}_3\text{NH}_3\text{I} \) modification can be understood, which is similar to the effect of surface modification observed in PSCs reported before [23, 31]. Figure 8d shows the plots for the ratio of shunt resistance (\( R_{\text{sh}} \)) to series resistance (\( R_{\text{s}} \)) and FF for the cells modified by \( \text{CH}_3\text{NH}_3\text{I} \) solutions with different concentrations. It is reported that the FF depends on the ratio of \( R_{\text{sh}} \) to \( R_{\text{s}} \) [38, 39]. The higher FF value for the cell modified by \( \text{CH}_3\text{NH}_3\text{I} \) solution is partially attributed to the large ratio of \( R_{\text{sh}} \) to \( R_{\text{s}} \). In short, this PSC modified at the optimal process has the highest \( J_{\text{sc}} \), \( V_{\text{oc}} \), and FF, thus the best performances.

The PL spectra are usually used to explore the trap states and recombination properties of light-excited charge in semiconductors [23, 40–42]. Figure 9 shows the PL spectra of \( \text{CH}_3\text{NH}_3\text{PbI}_3\text{Cl}_x \) films deposited on bare TiO\(_2\) and modified TiO\(_2\) by \( \text{CH}_3\text{NH}_3\text{I} \) solutions with different concentrations. It can be seen that the peak position of the emission is consistent for all of the samples. However, their PL intensities vary a lot and increase with increase of the \( \text{CH}_3\text{NH}_3\text{I} \) concentration from 0 to 10 mg/ml, then decrease when the concentration increases to 20 mg/ml. The \( \text{CH}_3\text{NH}_3\text{PbI}_3\text{Cl}_x \) film deposited on bare TiO\(_2\) exhibits the highest intensity in PL spectra, corresponding to a higher charge recombination [23]. The \( \text{CH}_3\text{NH}_3\text{PbI}_3\text{Cl}_x \) film deposited on modified TiO\(_2\) by \( \text{CH}_3\text{NH}_3\text{I} \) with the concentration of 10 mg/ml shows the lowest peak intensity, indicating the lowest recombination rate [42] and thus the best
photovoltaic performance. This is consistent with the results obtained in EIS characterization (Fig. 8). It confirms that the CH$_3$NH$_3$I modification on the TiO$_2$ layer results in the reduction of recombination rate at the interface between the TiO$_2$ and CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$. The reduced recombination rate of photogenerated charges at the interface can contribute to the enhanced charge collection efficiency in the PSCs, resulting in the improved performance.

Conclusions

In summary, a series of PSCs based on the structure of glass/FTO/compact TiO$_2$/meso-TiO$_2$/CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$/spiro-OMeTAD/Ag have been fabricated. CH$_3$NH$_3$I are used to modify the interface between meso-TiO$_2$ and CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$. It has been revealed that modifying the interface by CH$_3$NH$_3$I with appropriate concentration can significantly improve the performance of PSCs. After the CH$_3$NH$_3$I modification, the PCE of PSCs increases to 12.27 from 9.68 % of the references device. It is suggested that the better performance for CH$_3$NH$_3$I modified device is mainly attributed to the improved crystalline property, increased sunlight absorption in the visible range and reduced charge recombination rate.

Additional file

**Additional file 1: Figure S1.** The Nyquist plots of PSCs modified by CH$_3$NH$_3$I solution with different concentrations, measured at the bias voltage of $-0.8$ V (close to $V_{oc}$) in the dark. The plots in (a) and (c) correspond to the amplified spectra of (b) and (d) in the high frequency range, respectively. The two R-CPE circuits in series are employed to fit the experimental data in (a) and (b). Only one R-CPE circuit is used to fit the data in (c) and (d). The solid lines are the fittings of the experimental data. It can be seen that the experimental data can be better fitted in Figure S1(a) and S1(b) than that in Figure S1(c) and S1(d). This confirms that the Nyquist plots consist of two semicircles. (TIF 168 kb)

Competing interests

The authors declare that they have no competing interests.
Authors’ contributions

SWJ proposed the idea and designed the experiments. WW performed the experiments, analyzed results, and drafted the manuscript. ZBJ, YYC, JSC, JMWW, and RYH participated in the sample fabrication and characterizations. XSG, XBL, and LLS contributed to the data interpretation. SWJ and JML contributed to the data interpretation, manuscript writing, and supervised the research. All authors read and approved the final manuscript.

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