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Effects of precursor solution composition on the performance and I-V hysteresis of perovskite solar cells based on $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$

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Abstract

Precursor solution of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ for perovskite solar cells was conventionally prepared by mixing PbCl_2 and $\text{CH}_3\text{NH}_3\text{I}$ with a mole ratio of 1:3 ($\text{PbCl}_2:\text{CH}_3\text{NH}_3\text{I}$). While in the present study, $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ -based solar cells were fabricated using the precursor solutions containing PbCl_2 and $\text{CH}_3\text{NH}_3\text{I}$ with the mole ratios of 1:3, 1.05:3, 1.1:3, and 1.15:3, respectively. The results display that the solar cells with the mole ratio of 1.1:3 present higher power conversion efficiency and less I-V hysteresis than those with the mole ratio of 1:3. Based on some investigations, it is concluded that the higher efficiency could be due to the smooth and pinhole free film formation, high optical absorption, suitable energy band gap, and the large electron transfer efficiency, and the less I-V hysteresis may be attributed to the small low frequency capacitance of the device.

Keywords: I-V hysteresis, Precursor solution composition, $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$

Background

Organometal halide perovskite solar cells (PSCs) have attracted much attention over the last several years due to their outstanding properties, such as large absorption coefficient, high electron-hole diffusion length, and high charge carrier mobility [1–6]. The power conversion efficiency (PCE) has increased from 3.8 to 22% [7]. The typical architectures of PSCs mainly contain electron transporting layer (ETL)/perovskite/hole transporting layer (HTL) (n-i-p) and HTL/perovskite/ETL (p-i-n) structures [8]. In the $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($X = \text{I}, \text{Br}, \text{Cl}$) family, a mixed halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ ($\text{MAPbI}_{3-x}\text{Cl}_x$) has been proved a large diffusion length ($\sim 1 \mu\text{m}$), which could be applied for planar heterojunction solar cells with improved device performance [9, 10]. Some groups have reported the results of the $\text{MAPbI}_{3-x}\text{Cl}_x$ -based solar cells [11–13], in which the highest PCE is 19.3% [14].

The precursor solution of $\text{MAPbI}_{3-x}\text{Cl}_x$ is conventionally prepared by mixing PbCl_2 and $\text{CH}_3\text{NH}_3\text{I}$ with a mole ratio of 1:3 ($\text{PbCl}_2:\text{CH}_3\text{NH}_3\text{I}$). While there was no or only trace amount of Cl to be detected [15, 16]. Some studies have been performed to investigate the role of Cl in the $\text{MAPbI}_{3-x}\text{Cl}_x$ film formation [17, 18]. A widely accepted opinion is that Cl ion in organometal halide perovskite can boost the mobility of excitons and the charge carrier transport [19–21]. A few groups have fabricated $\text{MAPbI}_{3-x}\text{Cl}_x$ solar cells using the precursor solutions containing excess PbCl_2 to investigate its effect on the performance of solar cells based on the I-V measurement with single scan direction [18, 21–23]. It has been reported that hysteretic effects were observed during the I-V measurement of the perovskite solar cells [24]. I-V hysteresis could lead to an over- or underestimation of the PCE if it is not considered. Up to now, there are few reports to investigate the effects of excess PbCl_2 on the PCE and I-V hysteresis of $\text{MAPbI}_{3-x}\text{Cl}_x$ solar cells by considering the hysteretic effect.

Therefore in the present study, $\text{MAPbI}_{3-x}\text{Cl}_x$ -based solar cells were fabricated using the precursor solutions containing different mole ratios of PbCl_2 , and $\text{CH}_3\text{NH}_3\text{I}$.

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I-V measurements were carried out with reverse scan (RS) and forward scan (FS). The photovoltaic parameters were obtained from the I-V curves averaged with RS and FS. Based on the measurements, the effects of excess PbCl_2 on the PCE and the I-V hysteresis of the solar cells were investigated. One of the novelties of this work is that the photovoltaic parameters were obtained by an average of RS and FS to improve the accuracy of data. The other is the observation and investigation of the effect of excess PbCl_2 on I-V hysteresis.

Methods

Materials preparation

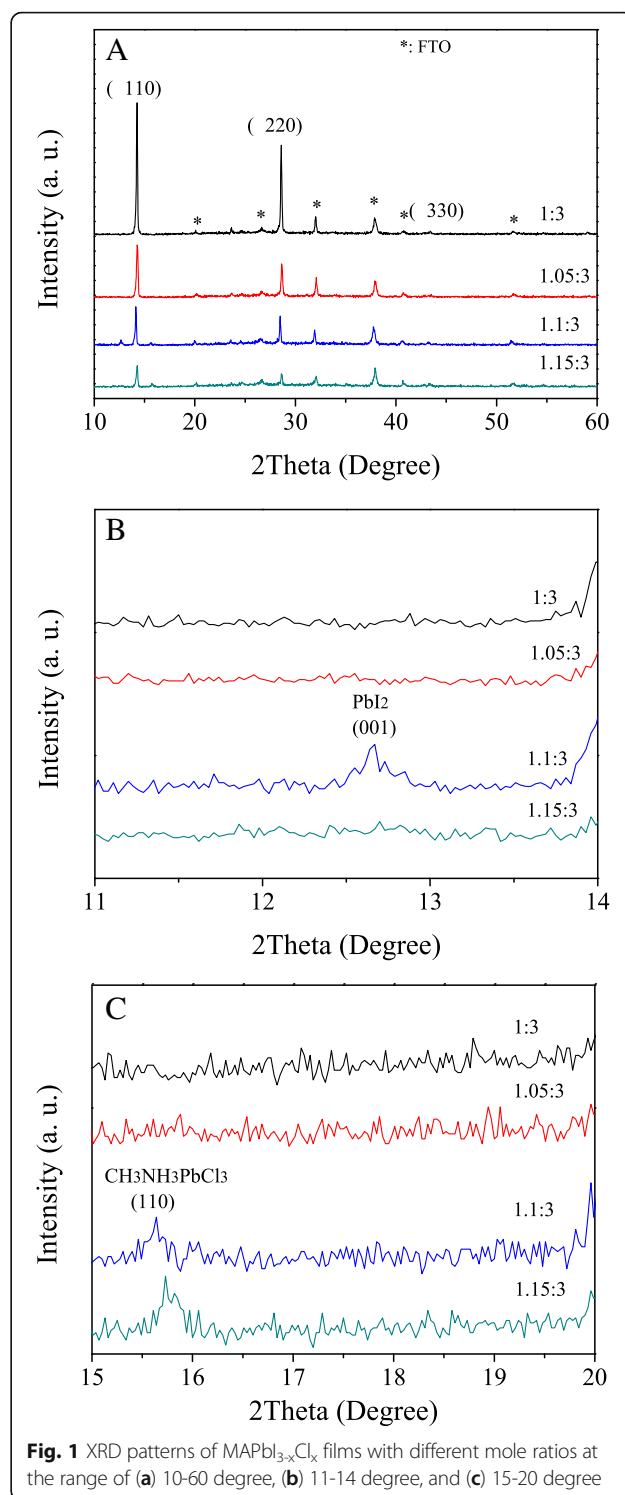
Methylammonium iodide ($\text{CH}_3\text{NH}_3\text{I}$) was synthesized with a method reported in the literature [25]. The perovskite precursor solutions (40 wt%) were obtained by mixing PbCl_2 and $\text{CH}_3\text{NH}_3\text{I}$ (MAI) in anhydrous *N,N*-Dimethylformamide (DMF) at 60 °C with the mole ratios of 1:3, 1.05:3, 1.1:3, and 1.15:3 (PbCl_2 to MAI), respectively.

Solar cell fabrication

Perovskite solar cells with a structure of n-i-p were fabricated. FTO-coated glass substrate (~15 ohm/sq, NPG, Japan) was patterned and cleaned with detergent, acetone, 2-propanol, and ethanol for 15 min by sonication. Then the substrate was treated by oxygen plasma for 20 min. A hole-blocking layer of compact TiO_2 was deposited by spin-coating, a mildly acidic solution of titanium isopropoxide (Aladdin reagent) in ethanol (350 μl in 5 ml ethanol with 0.013 M HCl) at 2000 rpm for 30 s and annealed at 500 °C for 30 min. A mesoporous TiO_2 layer composed of commercial TiO_2 paste (Dyesol 18NRT, Dyesol) diluted in ethanol (1:3.5, weight ratio) was then deposited on the top of compact layer by spin-coating at 5000 rpm for 30 s. After drying at 125 °C, the TiO_2 films were annealed at 500 °C for 30 min. The perovskite precursor solution was spin-coated on the mesoporous TiO_2 film at 2000 rpm for 45 s in an argon-filled glove box. The sample was dried on a hotplate for 60 min at 110 °C. The hole-transporter layer was formed by spincoating a spiro-OMeTAD solution at 2000 rpm for 45 s. Finally, a gold layer with the thickness of 80 nm was deposited on top of the device by thermal evaporation in air.

Characterization

X-ray diffraction (XRD) patterns were carried out on a DX-2700 diffractometer. UV-vis absorption spectra were performed on a UV-vis spectrophotometer (Varian Cary 5000). Morphologies and microstructures were obtained by a scanning electron microscope (SEM, JEM-7001 F, JEOL). Photocurrent-voltage (I-V) curves were carried out with a Keithley 2440 Sourcemeter under AM 1.5 G illumination with 100-mW/cm² intensity from a



Newport Oriel Solar Simulator. The active area of the device was 0.1 cm² determined with a mask. Steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectra were collected using a fluorometer (FLS 980E, Edinburgh Photonics). Capacitance-frequency measurements were performed under a forward bias of

0.6 V under 1 sun illumination conditions using an electrochemical workstation (RST5200, Zhengzhou Shiruisi Instrument Co., Ltd.) with the frequency range from 0.1 to 1000 Hz. The electrochemical impedance (IS) measurements were carried out with an electrochemical workstation (CHI660e, Shanghai CHI Co., Ltd.) in the frequency range from 0.1 to 100 kHz, in which an alternative signal with 5 mV magnitude was applied.

Results and discussion

Figure 1 shows the XRD patterns of $\text{MAPbI}_{3-x}\text{Cl}_x$ films with different mole ratios. Three main diffraction peaks at about 14.2° , 28.6° , and 43.1° are ascribed to (110), (220), and (330) lattice planes of halide perovskite with a tetragonal structure [26]. This indicates that the perovskite films with tetragonal structure are formed. A weak peak located at 12.7° for the sample with the ratio of 1.1:3 (Fig. 1b) can be assigned to the (001) diffraction peak of PbI_2 [10]. The peak at about 15.6° for the samples with the mole ratios of 1.1:3 and 1.15:3 (Fig. 1c) can be assigned to the (110) diffraction peak of $\text{CH}_3\text{NH}_3\text{PbCl}_3$ [18]. This agrees with the previous reports that Cl incorporation in an iodide-based structure was only at low concentration, and phase separation readily occurred with increased concentration [22, 27]. The PbI_2 phase appeared for the sample with the mole ratio of 1.1:3 and then disappeared for that with the mole ratio of 1.15:3 (Fig. 1b). While the $\text{CH}_3\text{NH}_3\text{PbCl}_3$ phase appeared in both the samples with the mole ratios of 1.1:3 and 1.15:3 (Fig. 1c). This is in accord with the reported $\text{MAPbI}_{3-x}\text{Cl}_x$ film growth process [23]. As a nucleation center, PbCl_2 induces the nucleation of PbI_2 . PbI_2 acts with MAI to form the perovskite film and exhausts the available Pb ions to form $\text{CH}_3\text{NH}_3\text{PbCl}_3$.

Figure 2a shows the UV-vis absorption spectra of $\text{MAPbI}_{3-x}\text{Cl}_x$ films with different mole ratios. The absorption intensity increases firstly, and then decreases with the increase of mole ratio, which is the strongest at the mole ratio of 1.1:3. Figure 2b shows the absorption spectra of $\text{MAPbI}_{3-x}\text{Cl}_x$ films at the range from 730 to 800 nm. The absorption edge is obtained by extrapolating from the absorption of direct transition [28]. The

band gap of $\text{MAPbI}_{3-x}\text{Cl}_x$ can be estimated from the absorption edge to be 1.573, 1.580, 1.598, and 1.596 eV for $\text{MAPbI}_{3-x}\text{Cl}_x$ with the mole ratio of 1:3, 1.05:3, 1.1:3, and 1.15:3, respectively.

Figure 3 shows the SEM images of the $\text{MAPbI}_{3-x}\text{Cl}_x$ films with different mole ratios. It is observed that some needle-like crystals for the film with the mole ratio of 1:3 (Fig. 3a). The films with the mole ratios of 1.05:3 and 1.15:3 become smooth and cover all the substrate with some small pinholes (Fig. 3b, d). At the mole ratio of 1.1:3, the pinholes disappeared and the substrate was fully covered by the $\text{MAPbI}_{3-x}\text{Cl}_x$ film (Fig. 3c). According to the previous reports [23, 29], PbCl_2 colloids in the precursor solution act as heterogeneous nucleation sites for the perovskite film formation. When excess PbCl_2 was introduced, the heterogeneous nucleation sites increased rationally, which possibly enhanced the morphology eventually. As the amount of PbCl_2 further increased, the grain size of the perovskite film slightly increased, and the surface becomes smoother.

Figure 4a shows the PL spectra of $\text{MAPbI}_{3-x}\text{Cl}_x$ films with different mole ratios on FTO substrate. The peak at ~ 780 nm could be from the emission of $\text{MAPbI}_{3-x}\text{Cl}_x$ [9]. The PL intensities of the films with the mole ratios of 1.05:3, 1.1:3, and 1.15:3 are higher than that of 1:3. The TRPL spectra of $\text{MAPbI}_{3-x}\text{Cl}_x$ films with different mole ratios on FTO substrate are shown in Fig. 4b. The TRPL curve was fitted with an exponential diffusion model, and the exciton lifetime is 58, 79, 67, and 177 ns for the perovskite film with the mole ratio of 1:3, 1.05:3, 1.1:3, and 1.15:3, respectively. The exciton lifetimes of the films with the mole ratio of 1.05:3, 1.1:3, and 1.15:3 are longer than that of that of 1:3. The higher PL intensities could be due to their longer exciton lifetimes [30, 31].

The enhanced exciton lifetime indicates the reduced recombination in the $\text{MAPbI}_{3-x}\text{Cl}_x$ films. To investigate the charge transfer between $\text{MAPbI}_{3-x}\text{Cl}_x$ film and TiO_2 , the PL spectra of $\text{FTO}/\text{TiO}_2/\text{MAPbI}_{3-x}\text{Cl}_x$ samples were performed and shown in Fig. 4c. Compared with the PL spectra of $\text{FTO}/\text{MAPbI}_{3-x}\text{Cl}_x$ (Fig. 4a), there is a quenching effect when the $\text{MAPbI}_{3-x}\text{Cl}_x$ layer contacts

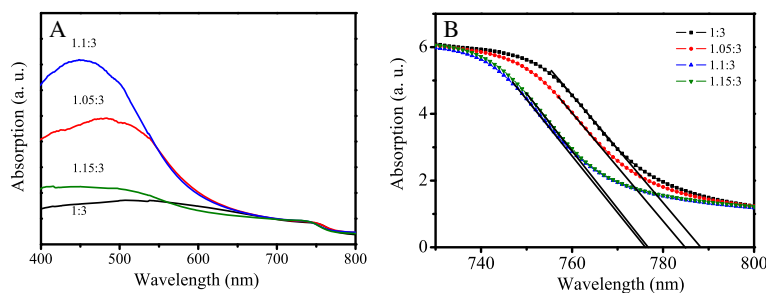


Fig. 2 UV-vis absorption spectra of $\text{MAPbI}_{3-x}\text{Cl}_x$ films with different mole ratios at the range of (a) 400–800 nm, and (b) 730–800 nm

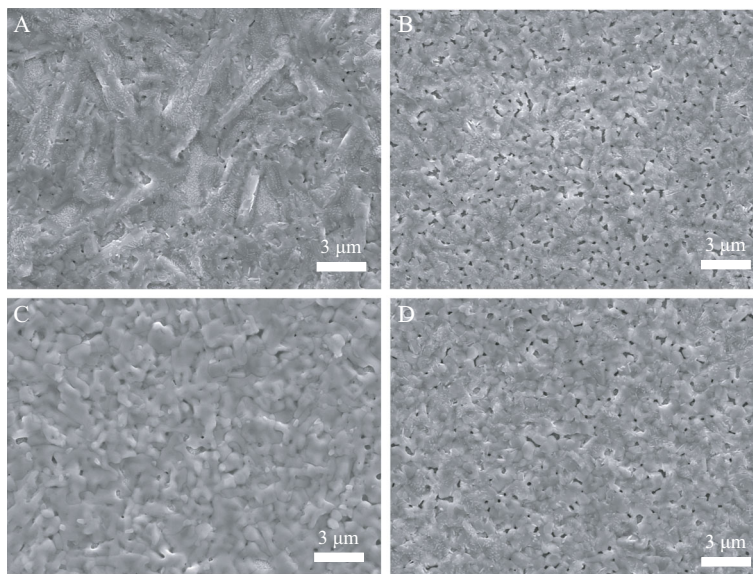


Fig. 3 SEM images of the MAPbI_{3-x}Cl_x films with the mole ratio of (a) 1:3, (b) 1.05:3, (c) 1.1:3, and (d) 1.15:3

with TiO₂ film, which is due to the electron injection from MAPbI_{3-x}Cl_x to TiO₂. The charge transfer efficiency can be estimated by the PL intensity ratio of FTO/TiO₂/MAPbI_{3-x}Cl_x to FTO/MAPbI_{3-x}Cl_x, which is 0.25, 0.21, 0.19, and 0.24 for the perovskite films with the mole ratio of 1:3, 1.05:3, 1.1:3, and 1.15:3, respectively. The PL intensity ratio of the sample with the mole ratio of 1.1:3 is

smaller than the others, which indicates a more efficient electron transfer to TiO₂. This could be due to a stronger interfacial coupling at the interface [32].

Perovskite solar cells were fabricated using the precursor solutions with different mole ratios with a structure of FTO/c-TiO₂/mp-TiO₂/MAPbI_{3-x}Cl_x/spiro-oMeTAD/Au. Figure 5 shows the photovoltaic parameters of the solar

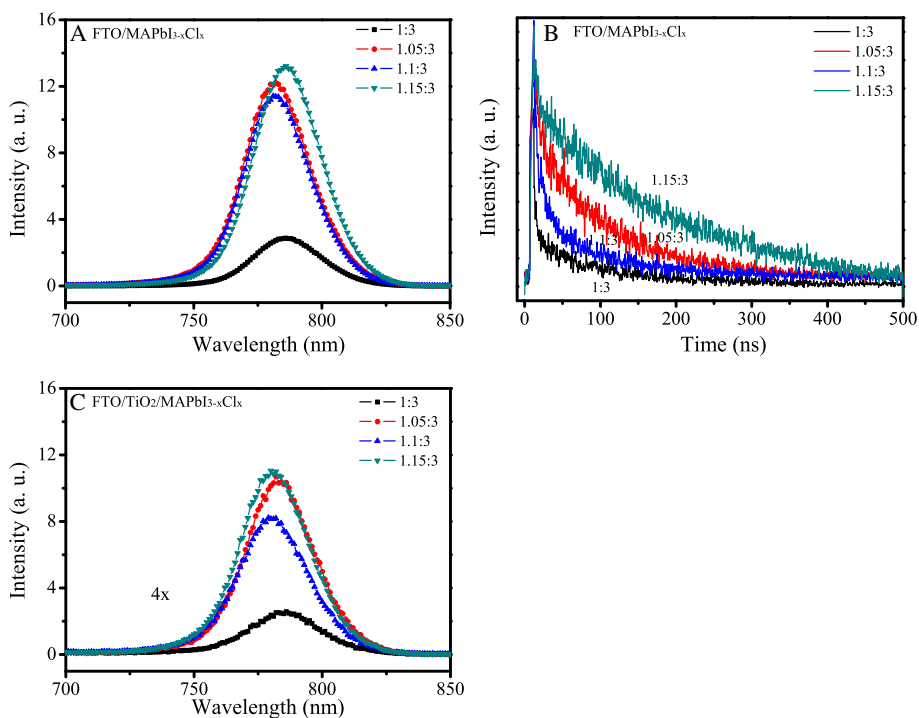


Fig. 4 a PL and b TRPL spectra of FTO/MAPbI_{3-x}Cl_x samples. c PL spectra of FTO/TiO₂/MAPbI_{3-x}Cl_x samples

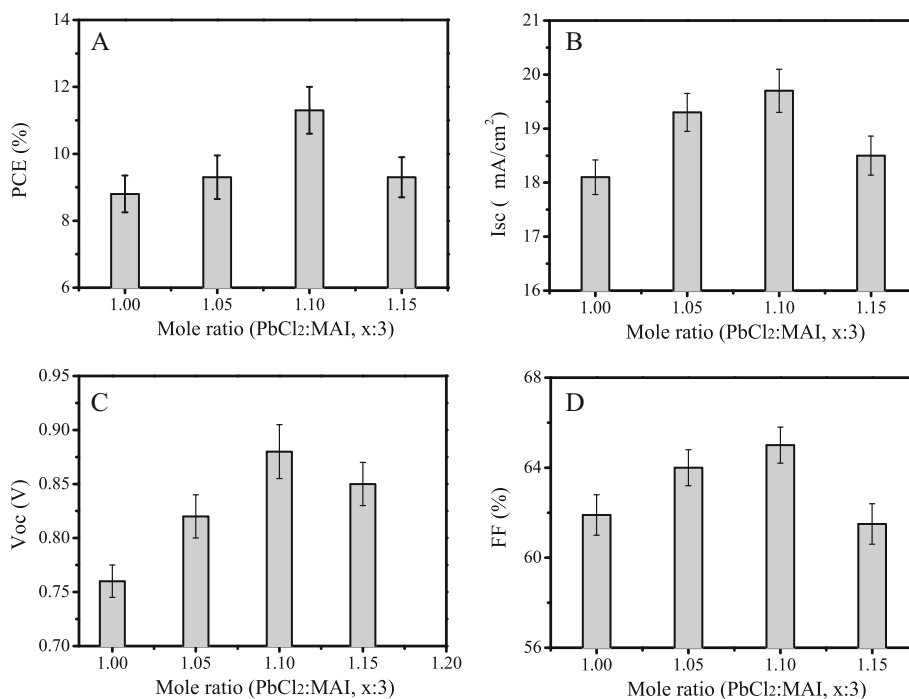


Fig. 5 Photovoltaic parameters of the solar cells using the precursor solutions with different mole ratios. **a** J_{sc} , **b** V_{oc} , **c** FF, and **d** PCE. The data were obtained from 20 pieces of devices for each of precursor solutions

cells, which were obtained from 20 pieces of devices for each of precursor solutions. The short current (J_{sc}), open voltage (V_{oc}), fill factor (FF) and power conversion efficiency (PCE) were obtained from I-V curves averaged with reverse scan (RS) and forward scan (FS). These parameters are listed in Table 1. With the increase of mole ratio, the parameters of the solar cells were firstly increased, and then decreased. The solar cells with the mole ratio of 1.1:3 present an enhanced performance. Compared with those of solar cells with the mole ratio of 1:3, the V_{oc} , J_{sc} , FF, and PCE of the solar cells with the mole ratio of 1.1:3 were increased to 0.88 V, 19.7 mA/cm², 65%, and 11.3% from 0.76 V, 18.1 mA/cm², 61.9%, and 8.8%, respectively.

Figure 6 shows the current density-voltage (I-V) curves of the best solar cells using the precursor solutions with different mole ratios. It was found that the degree of I-V hysteresis depends on the precursor composition. This phenomenon was always observed in

our experiments. I-V hysteresis index (HI) is defined by the following equation [33],

$$\text{hysteresis index} = \frac{J_{RS}(0.8V_{oc}) - J_{FS}(0.8V_{oc})}{J_{RS}(0.8V_{oc})}$$

where $J_{RS}(0.8V_{oc})$ and $J_{FS}(0.8V_{oc})$ stand for the photocurrent density at 80% of V_{oc} for the RS and FS, respectively. The calculated hysteresis index values are 0.164, 0.085, 0.019, and 0.066 for the I-V curves with the mole ratio of 1:3, 1.05:3, 1.1:3, and 1.15:3, respectively. With the increase of mole ratio, the hysteresis degree first decreases, and then increases. At the mole ratio of 1.1:3, the hysteresis index value is the smallest. The high PCE of 11.55% with less I-V hysteresis was obtained using the precursor solution with the mole ratio of 1.1:3.

To get an insight into the enhanced performance and less I-V hysteresis of the solar cells with the mole ratio of 1.1:3, some investigations were performed. Based on the energy band gaps calculated from the absorption spectra (Fig. 2) and the literature [33], the energy band diagrams of TiO₂, MAPbI_{3-x}Cl_x, and Spiro-OMeTAD are shown in Fig. 7. The conduction band offset between MAPbI_{3-x}Cl_x and TiO₂ is the largest for the mole ratio of 1.1:3 due to its wide band gap, which might be one of the reasons to present a higher voltage [28]. Moreover, the larger conduction band offset might contribute to its increased current density, because the band offset has

Table 1 Photovoltaic parameters of perovskite solar cells as a function of different mole ratios of PbCl₂ and MAI

PbCl ₂ :MAI	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	η (%)
1:3	0.76 ± 0.01	18.1 ± 0.2	61.9 ± 1.6	8.8 ± 0.1
1.05:3	0.82 ± 0.02	19.3 ± 0.3	64.0 ± 1.5	9.3 ± 0.2
1.1:3	0.88 ± 0.01	19.7 ± 0.1	65.0 ± 0.5	11.3 ± 0.2
1.15:3	0.85 ± 0.01	18.5 ± 0.2	61.5 ± 1.5	9.3 ± 0.3

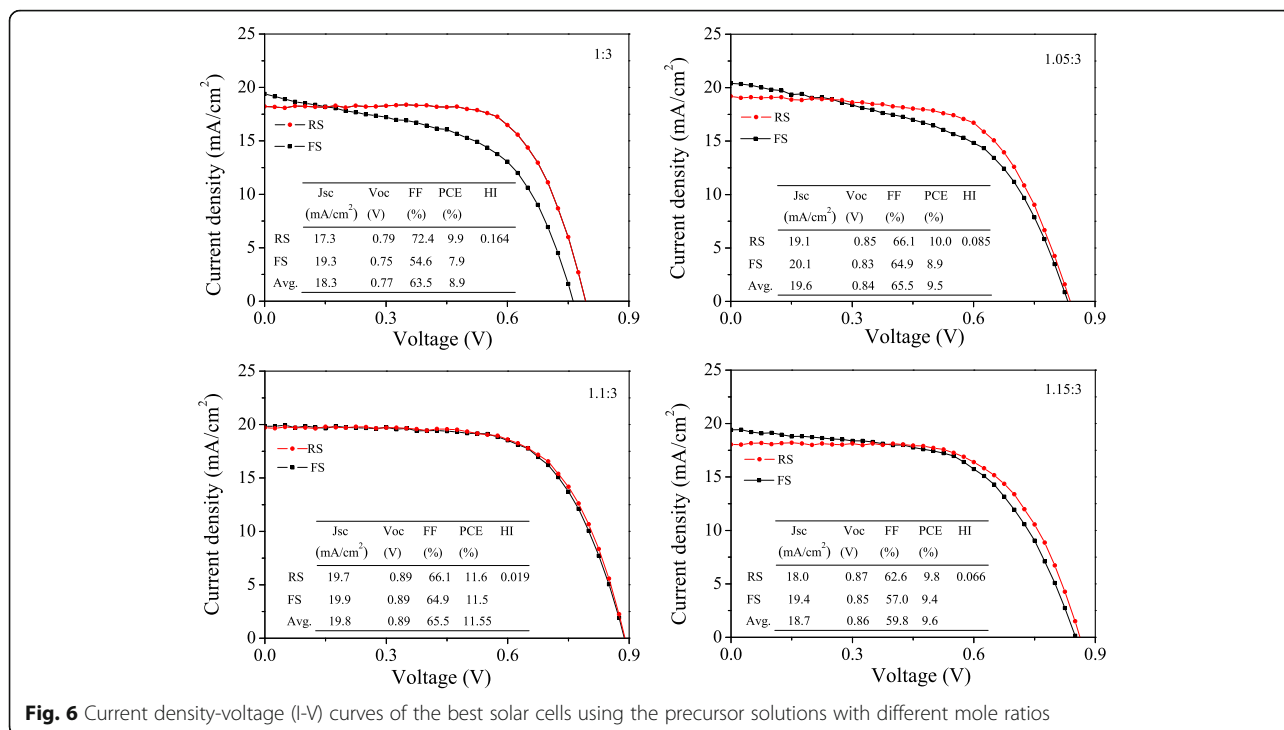


Fig. 6 Current density-voltage (I-V) curves of the best solar cells using the precursor solutions with different mole ratios

been proved to be a driving force for charge transfer between conduction bands in the heterojunction [34, 35]. This speculation was confirmed by the photoluminescence (PL) results.

Hysteretic effects during I-V measurements have been observed in perovskite solar cells. It has been proposed that the slow decay process of the capacitive charging or discharging current during voltage sweep induces the non-steady state photocurrent and I-V hysteresis [33, 36, 37]. The non-steady state photocurrents could be due to the capacitance at low frequency (0.1 ~ 1 Hz) resulting from electrode polarization at perovskite/electrode interfaces [33]. To understand the I-V hysteresis of the solar cells with different precursor compositions, the capacitance of the

devices were directly measured with an electrochemical workstation. Figure 8 shows the dependence of capacitance on frequency. The low frequency capacitance (C_{LF}) is observed near 10^{-1} Hz. With the increase of the mole ratio, C_{LF} decreases firstly, and then increases, which is the smallest at the mole ratio of 1.1:3. The smaller C_{LF} indicates the less polarization which could be the origin of the I-V hysteresis [33]. The variation of C_{LF} with the mole ratio agrees with the I-V hysteresis tendency shown in Fig. 4.

To investigate the reason of capacitance decrease, the impedance spectra of the solar cells were measured. Figure 9a shows the Nyquist plots of the cells based on

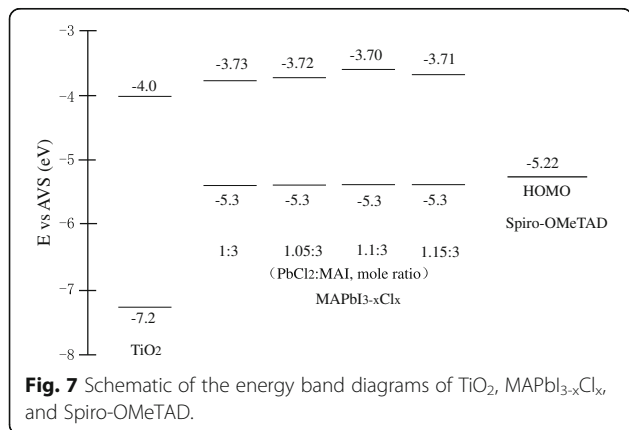


Fig. 7 Schematic of the energy band diagrams of TiO₂, MAPb_{13-x}Cl_x, and Spiro-OMeTAD.

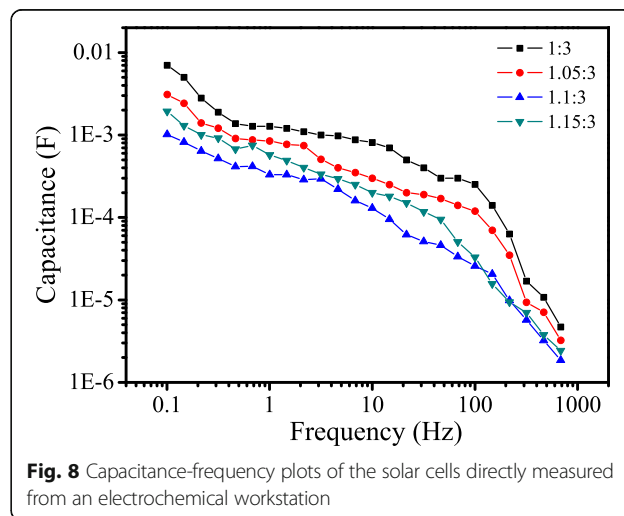
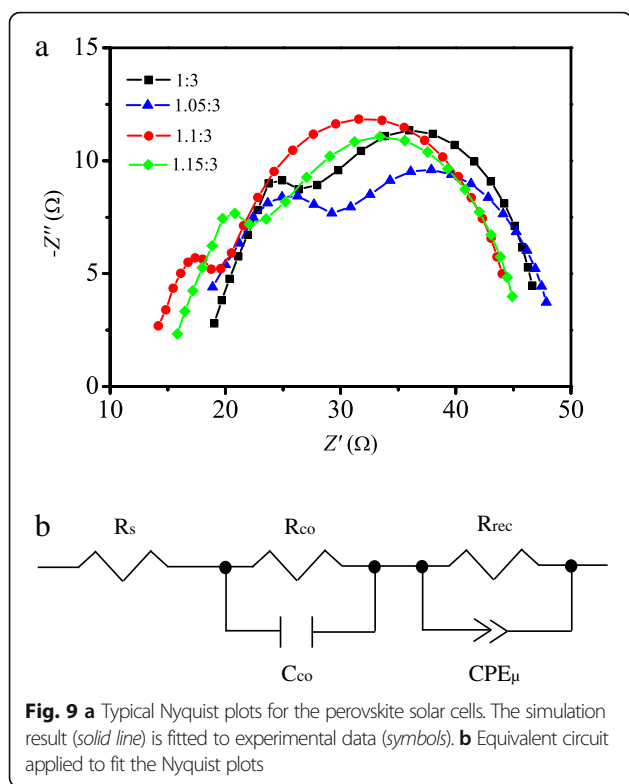


Fig. 8 Capacitance-frequency plots of the solar cells directly measured from an electrochemical workstation



the different mole ratios, in which the symbols are the experimental data and the solid lines are the fitting results. There are two RC arcs contained in the plots. Figure 9b shows the equivalent circuit used to fit the data. The high-frequency RC element could be ascribed to the contact resistance (R_{co}) at the interfaces, while the low-frequency element may be attributed to the recombination resistance (R_{rec}) and chemical capacitance (C_{μ}) of the device, and the R_s is a series resistance [38]. The parameters obtained by fitting are listed in Table 2. The R_{co} (10.6 Ω) of solar cells based on precursor solution with mole ratio of 1.1:3 is smaller than that of the other precursor solution. This indicates that the perovskite film with the mole ratio of 1.1:3 provides better contact with electron transporting layer and hole transporting layer than the other perovskite film. Thus, the decreased capacitance of the solar cells with the mole ratio of 1.1:3 could be due to the better contact of perovskite film with ETL and HTL [39].

Table 2 Fitting parameters for EIS data

Sample	R_s/Ω	R_{co}/Ω	R_{rec}/Ω	C_{co}/F	$CPE-T/F$
1:3	17.7	21.0	23.7	1.5E-7	3.6E-6
1.05:3	17.1	17.8	27.5	1.6E-8	2.5E-6
1.1:3	13.5	10.6	28.5	1.2E-7	6.9E-7
1.15:3	15.2	16.8	27.6	1.3E-7	5.1E-6

Conclusion

The solar cells based on $MAPbI_{3-x}Cl_x$ were fabricated using the precursor solutions containing the mole ratio of 1:3, 1.05:3, 1.1:3, and 1.15:3. I-V curves were obtained by both reverse scan and forward scan, from which the photovoltaic parameters were calculated by taking the average of them. The results displayed that the solar cells with the mole ratio of 1.1:3 present higher PCE and less I-V hysteresis. To get an insight into the results, some investigations were performed. The higher PCE could be due to the smooth and pinhole-free film formation, high optical absorption, suitable energy band gap, and the large electron transfer efficiency. The less I-V hysteresis may be attributed to the small low frequency capacitance of the device.

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Authors' contributions

Z-LZ, B-QM, and Y-LM carried out the main part of experiment and drafted the manuscript. Other authors provided assistance with experimental measurements, data analysis, and the manuscript writing. All authors read and approved the final manuscript.

Competing interests

The authors declare that they have no competing interests.

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