Perfection of Perovskite Grain Boundary Passivation by Rhodium Incorporation for Efficient and Stable Solar Cells

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HIGHLIGHTS

• Rhodium ion incorporation helps the nucleation of perovskite grain, passivates the defects in the grain boundaries and enhances the film quality, charge carrier lifetime and mobility.

• After optimizing 1% rhodium into perovskite film, the solar cells achieve an efficiency of 20.71% without obvious hysteresis.

ABSTRACT

Organic cation and halide anion defects are omnipresent in the perovskite films, which will destroy perovskite electronic structure and downgrade the properties of devices. Defect passivation in halide perovskites is crucial to the application of solar cells. Herein, tiny amounts of trivalent rhodium ion incorporation can help the nucleation of perovskite grain and passivate the defects in the grain boundaries, which can improve efficiency and stability of perovskite solar cells. Through first-principle calculations, rhodium ion incorporation into the perovskite structure can induce ordered arrangement and tune bandgap. In experiment, rhodium ion incorporation with perovskite can contribute to preparing larger crystalline and uniform film, reducing trap-state density and enlarging charge carrier lifetime. After optimizing the content of 1% rhodium, the devices achieved an efficiency up to 20.71% without obvious hysteresis, from 19.09% of that pristine perovskite. In addition, the unencapsulated solar cells maintain 92% of its initial efficiency after 500 h in dry air. This work highlights the advantages of trivalent rhodium ion incorporation in the characteristics of perovskite solar cells, which will promote the future industrial application.

KEYWORDS Perovskite solar cells; Grain boundary passivation; Rhodium incorporation
1 Introduction

Halide perovskites have attracted great attention owing to the eminent optoelectronic properties, such as suitable energy bandgap [1–6], high absorption coefficient [7–9], long charge diffusion length [10–13] and high carrier mobility [14, 15]. Those advantages boost the improvement in perovskite solar cells (PSCs), being with certified power conversion efficiency (PCE) up to 25.2% [16].

However, pristine perovskite has inevitable internal defects, such as Pb and I vacancy defects, especially in gain boundary, which reduce the performance and stability of PSCs. To date, doping metal ion is an effective strategy to reduce defects, which can improve efficiency and stability of PSCs [17]. For example, doping with monovalent metal cations (Cu+, Ag+ or Li+) was applied to reduce trap-state density [18, 19], improved perovskite crystallinity and film quality, thus enhanced performance of PSCs. By doping bivalent cations (Mn2+, Co2+ or Zn2+), tuned electronic band structures and crystalline morphology were received and improved the stability of PSCs [20–27]. Trivalent metal cations (In3+, Eu3+ and Al3+) were often used to decrease deep defects, optimize film morphology and increase efficiency and stability of PSCs [28–31]. Especially for Eu3+ doping, device achieves long-term durability with 92% of the original PCE under continuous illumination for 1500 h [31]. Hence, finding more trivalent metal ions to obtain excellent properties of PSCs is important. The radius of Rh3+ is 67 pm, which is less than Pb2+ (119 pm). A smaller radius allows both interstitial doping and the possibility of partial replacement of Pb2+. Moreover, 4d orbital of Rh3+ probably tunes electrical properties of perovskite films by heterovalent incorporation [32, 33]. Clearly, compared to elements doped without d orbitals (such as, Al3+), such method definitely advances hybrid perovskite materials [30]. Therefore, it is anticipated that Rh3+ can be used in hybrid perovskite to enhance the properties of devices.

Here, we utilized Rh3+ to be incorporated with MAPbI3 for developing MAPbI3:Rh3+ (where x is excessive rhodium mol ratio, and x = 0, 0.5, 1.0 and 5.0 mol%). Rh3+ incorporation with tiny amounts can help the nucleation of perovskite grain and passivate the defects in perovskite film boundaries. In addition, 1% Rh3+ incorporation with perovskite films possesses larger crystalline and less pinhole, which leads to reduce trap-state density and enlarge charge carrier lifetime. Planar heterojunction PSCs with 1% Rh3+ incorporation exhibit high PCE of 20.71% and significantly suppressed photocurrent hysteresis. Compared to other studies of PSCs, the PSCs based on Rh3+ incorporation MAPbI3 achieved higher PCE (Table S11). Meanwhile, the devices of 1% Rh3+ incorporation have high stability within 500 h without encapsulation in dry air. This work highlights the advantages of Rh3+ incorporation in PSCs, which can promote the future industrial application.

2 Experimental Section

2.1 First-Principle Calculation

All of the density functional theory (DFT) calculations were employed by VASP code [34]. Generalized gradient approximation (GGA) of the projector augmented wave (PAW) was employed [35]. The plane-wave energy cutoff is 500 eV. The energy cutoff convergence is $1 \times 10^{-4}$ eV, and the force cutoff convergence is $-0.09$ eV Å$^{-1}$ [36, 37]. For perovskite structure, 3×3×3 Monkhorst–Pack grid is taken [38]. The results of calculated lattice constants are well agreed with the experimental from Rietveld refinement (Table S2).

2.2 Preparation of Perovskite Single Crystals

For MAPbI3 single crystal, PbI2 (2.835 g) and MAI (0.978 g) were mixed in 5 mL γ-butyrolactone under stirring at 70 °C for 2 h. After heating the solution at 150 °C for 24 h, some obvious single crystals were obtained, which were washed with γ-butyrolactone and dried at 50 °C. Select a relatively large single crystal as the seed crystal, the above reaction was repeated once [11]. For MAPbI3:xRh (where x = 0.5, 1 and 5%) single crystal, x is excessive Rh3+ incorporation, and the mixed PbI2 and MAI solution was added 0.5, 1 and 5 mol% (0.015, 0.030 and 0.149 g) RhI3, respectively.

2.3 Preparation of Devices

SnO2 dense layer (2.67%, diluted by deionized water) was prepared for the cleaned ITO substrate by spin-coated method. For MAPbI3:xRh (where x = 0, 0.5, 1, 5%) solution, 159 mg MAI, 470 mg PbI2 and 0, 0.5, 1 and 5 mol %
(0, 2.42, 4.84 and 24.2 mg) RhI₃ were separately dissolved in 0.8 mL DMSO:DMF (1:4) solution under room temperature. In total, 35 μL perovskite solution dipped on the SnO₂ layers and then spun at 4000 rpm for 20 s. In total, 300 μL chlorobenzene was dipped on the substrate to enhance the film quality when the spinning at 10 s. Then, the substrate was annealed at hot plate. The hole transporting layer Spiro-OMeTAD was spin coated as our previous work [21]. Finally, the PSCs were evaporated 150 nm Ag (0.8 Å s⁻¹) with area of 0.09 cm².

3 Results and Discussion

The characteristics of device are closely related to the morphology of the absorption film. Figure 1 shows top-view SEM pictures of MAPbI₃⁺ₓRh (x = 0, 0.5%, 1% and 5%) (x represents Rh excessive incorporation). At low Rh³⁺-incorporated concentration, such as x = 0.5% and 1%, the grain size becomes larger than pristine MAPbI₃ film without Rh³⁺-incorporated (Fig. 1f, g). However, at high Rh³⁺-incorporated concentration (where x = 5%), the quality of film becomes worse (Fig. 1h). The phenomenon was explained both theoretically and experimentally. From the experimental perspective, when the Rh³⁺-incorporated concentration is 0.5% and 1%, the grain size becomes larger than pristine MAPbI₃ film without Rh³⁺-incorporated (Fig. 1f, g). However, at high Rh³⁺-incorporated concentration (where x = 5%), the quality of film becomes worse (Fig. 1h). The reason for this change in perovskite films is the different speed of film formation (Fig. 2). From a theoretical point of view, when the Rh³⁺-incorporated concentration of Rh³⁺ is 1%, Rh³⁺ through chemical bonds with the surrounding [PbI₆]⁴⁻ is to induce ordered arrangement and reduce defects [18]. However, when the Rh³⁺-incorporated concentration of Rh³⁺ is up to 5%, partial Rh³⁺ may replace Pb²⁺ to form additional perovskite structures. From intersecting surface SEM pictures of PSCs fabricated by MAPbI₃ and MAPbI₃⁺ₓRh (where x = 1%), there is no pinhole in the cross section after Rh³⁺ incorporation. This shows that Rh³⁺ incorporation makes both plane and cross section of perovskite continuous [39]. The film thicknesses with its deviations from (where x = 0, 1%) layers are 380 and 400 nm. Electron energy loss spectroscopy (EELS) mapping analysis of MAPbI₃⁺ₓRh (where x = 1%) shows that the atomic % is also similar to the ratio of experimental preparation (Table S1). From EELS mapping, most of rhodium atoms are distributed at the grain boundary. By grain boundary passivation of rhodium ions, larger perovskite grains without pinholes film were formed (Fig. 1g). In order to explore physical mechanism of MAPbI₃⁺ₓRh materials, we prepared the MAPbI₃⁺ₓRh (where x = 0, 0.5%, 1% and 5%) single crystal (Fig. S3). From Fig. 1k, l, XRD was measured to research the crystallinity of MAPbI₃⁺ₓRh single crystalline. The peaks of 14° and 28° that correspond to the (101) and (202) lattice planes can be clearly seen from XRD, which is indicated that the MAPbI₃⁺ₓRh possesses excellent crystallinity. No other peaks are observed for the MAPbI₃⁺ₓRh perovskites, which are indicated that the Rh³⁺ and Pb²⁺ cations have not formed different kinds of phases. Moreover, the diffraction angles are slight lessening when it is 0.5% Rh³⁺ incorporation MAPbI₃⁺ₓRh (Fig. 1k). The reason of that is the unit cell of MAPbI₃⁺ₓRh (where x = 0.5%) was enlarging from Rietveld refinement result (Table S2). However, when there is excessive 5% Rh³⁺ incorporation, the peak shift to a higher diffraction angle indicates the lattice parameters decrease. Maybe smaller Rh³⁺ cations partially displace the larger Pb²⁺ cations and the cell volume decreases (Table S2).

We set up the corresponding model and study electronic and optical properties of MAPbI₃⁺ₓRh (where x = 0, 6%, 8% and 12.5%) and MAPb0.875Rh0.125I₃ (Figs. 2 and S1, S5) based on the result of XRD Rietveld refinement. In perovskite system, iodide ion and methylamine ion are easy to dissociate, which is destroyed perovskite structure and resulted in iodine vacancy defect and methylamine ion vacancy defect. From first-principle calculation, the binding energy (formula as $E = E_{\text{doped}} - E_{\text{bulk}} - E_{\text{doping atom}}$) is ~3.45 eV [40]. indicating that Rh³⁺ can easily insert into the interstices of perovskite through the chemical bonds with iodine ion to enhance the stability of perovskite structure and prevent the ions from escaping and reduce iodine vacancy defects. Therefore, the crystallization of perovskite, tiny amount
of Rh\textsuperscript{3+} is near the octahedral [PbI\textsubscript{6}]\textsuperscript{4−} to induce ordered arrangement of organic cations to form high-quality film with few defects (Fig. 2a). From first-principle calculation, the bandgap values of MAPbI\textsubscript{3}:xRh (where x = 0, 6%, 8% and 12.5%) and MAPb\textsubscript{0.875}Rh\textsubscript{0.125}I\textsubscript{3} are 1.31, 1.84, 1.14, 0.80 and 1.15 eV, respectively. The calculated bandgap of 1.31 is similar to experimental bandgap of 1.57 eV. There is a small error in the results of experiment and calculation.

For the density of states (DOS) of MAPbI\textsubscript{3}, valence band maximum (VBM) and conduction band minimum (CBM) are mainly affected by orbitals hybridization of I and Pb. When rhodium ions are interstitial in perovskite structure, hybridization between rhodium and other atomic orbitals affects the distribution of DOS. From Fig. 2a, the rhodium atom makes the conduction band minimum move toward a higher energy level, thus increasing the bandgap. In Fig. 2b, DOS and band structure shows that the MAPbI\textsubscript{3} are nonmagnetic. From Fig. 2a, the spin-up and spin-down band structure is not imperfect symmetry, suggesting MAPbI\textsubscript{3}:xRh possesses magnetism. The calculated total magnetic moment of MAPbI\textsubscript{3}:xRh (where x = 6%) atom is 2.254 \mu B mainly attributed to Rh atom. This indicates the potential application of this material in the field of magnetism.

XPS was also further to verify Rh\textsuperscript{3+} incorporation and study chemical bonding states of the MAPbI\textsubscript{3}:xRh structure. Figure 3a shows a separation of approximately 11.6 eV from I 3d\textsubscript{5/2} and 3d\textsubscript{3/2} spectra. As the Rh concentration increased, the binding energy (BE) of I 3d is slightly toward higher. From Fig. 3b, the BE of the Pb 4f\textsubscript{7/2} was about 136.5 eV. As the Rh concentration is increased, the BE of Pb 4f is also slightly toward higher. This small transition to high binding energy may be the shorter Rh–I distance than Pb–I distance, which is lead to higher energy of Pb(Rh)–I bond. We can also observe from the Rietveld refinement above (Table S2). In addition, as the Rh\textsuperscript{3+}-incorporation concentration increases, the 1s orbital of N also moves to a higher binding energy. Stronger interactions of Rh–I bond can reduce iodine vacancy defects. The peak at 315 and 308 eV of MAPbI\textsubscript{3}:xRh (where x = 1%) film indicates the presence of Rh elements (Fig. 3d).

In order to study the distribution of energy level, absorbance coefficient and ultraviolet photoelectron spectroscopy (UPS) spectra were tested. When the Rh\textsuperscript{3+}-incorporated
concentration increased from 0 to 1%, the intensity of the absorption spectrum also increased. However, absorption intensity of 5% Rh³⁺ incorporation decreases, which may be related to the quality deterioration of perovskite films. We also calculated the absorption spectra, which were generally consistent with the experiment (Fig. S5a). The bandgap of MAPbI₃:ₓRh is calculated by converting the UV/Vis absorption spectrum into Tauc plots (Fig. 3g). On the basis of the Kubelka–Munk theory [21], the bandgap of MAPb₁₋ₓRh (where x = 0, 0.5%, 1% and 5%) is determined to be 1.570, 1.58, 1.58 and 1.59 eV, respectively. From Figs. 3f and S5a, with the increase of Rh³⁺-incorporated concentration, the absorption range was slightly blue shift and basically consistent with the increase of bandgap. Figure 3h shows UPS image of MAPb₁₋ₓRh (where x = 0, 0.5%, 1% and 5%). The specific energy levels were calculated from UPS and UV/Vis absorption (Fig. 3i). The formula for calculating the Fermi energy level is $E_F = 21.22 - E_B$ [21] (where $E_F$ is the Fermi level, and $E_B$ is high binding energy cutoff). The high binding energy cutoff of MAPb₁₋ₓRh is 16.89 eV. $E_F$ of MAPb₁₋ₓRh is −4.33 eV (21.22–16.89). The VBM of MAPb₁₋ₓRh is the $E_F$ minus low binding energy as −5.48 eV (−4.33–1.15). The CBM of MAPb₁₋ₓRh is the sum of VBM and bandgap as −3.91 eV. Other detail energy levels of MAPb₁₋ₓRh can be calculated in this way. Energy level diagram of MAPb₁₋ₓRh (where x = 0, 0.5%, 1% and 5%) is shown in Fig. 3i. The detailed analysis of energy levels is shown in Table S3.

The current density versus voltage ($J$–$V$) curve is important to study photovoltaic properties. $J$–$V$ curves of PSCs are fabricated by structure of ITO/SnO₂/MAPb₁₋ₓRh/Spiro-MeOTAD/Ag (Fig. 4a). Device photovoltaic parameters with MAPb₁₋ₓRh are shown in detail (Table 1). PSCs fabricated by pristine perovskite possess short-circuit current density ($J_{sc}$) of 22.46 mA cm⁻², open-circuit voltage ($V_{oc}$) of

![Fig. 2](image-url)
1.09 V, fill factor (FF) of 0.78, PCE of 19.09%. The PSCs prepared by MAPbI$_3$:Rh (where $x = 1\%$) possess high PCE of 20.71% (Table 1), which is increased approximately 10% compared to that of based on MAPbI$_3$. However, the properties of PSCs based on MAPbI$_3$:xRh (where $x = 5\%$) have decreased. The MAPbI$_3$:xRh (where $x = 5\%$) films possess poor-quality films, which leads to large leakage current, low $J_{sc}$. To ensure repeatability of device performance, over 40 PSCs are fabricated and characterized (Tables S5–S8). PSCs based on MAPbI$_3$ show a wide photoresponse in the range of 350–800 nm, and external quantum efficiency (EQE) values were close to 85%. EQE values of devices fabricated by 1% Rh incorporation are risen to more than 90%. The photocurrent of 21.62, 22.13, 23.37 and 21.00 mA cm$^{-2}$ is obtained by integration of EQE spectrum in the range of 350–800 nm, which is similar to the $J_{sc}$ from the results of $J$–$V$ measurement.

Charge transfer characteristics of PSCs were studied by electrochemical impedance spectroscopy (EIS). The EIS was tested in the dark under applied bias of $V_{OC}$. Under such a condition, the charge carrier recombination resistance ($R_{REC}$) attained the lowest value ($R_{REC} \ll R_{CT}$), and $R_{CT}$ is the charge transfer resistance. Semicircle from EIS measurement is formed by series resistor ($R_s$), charge transport

![Fig. 3 XPS of a 1 3d, b Pb 4f, c N 1s from MAPbI$_3$:xRh (where $x = 0$, 0.5%, 1% and 5%). d Rh 4d from MAPbI$_3$:xRh (where $x = 1\%$). e XPS of total elements from the MAPbI$_3$:xRh (where $x = 1\%$). f Absorbance coefficient of MAPbI$_3$:xRh. g Estimated bandgap potential of perovskite films. h UPS of MAPbI$_3$:xRh (where $x = 0$, 0.5%, 1% and 5%). i Energy level diagram of MAPbI$_3$:xRh (where $x = 0$, 0.5%, 1% and 5%).]
resistor ($R_{ct}$) and capacitor (CPE1). The inset of Fig. 4d is equivalent circuit diagram [41]. Because all devices have the same structure, $R_S$ values are basically the same (Fig. S6). The radius of the arc represents the value level of $R_{ct}$.

The lowest $R_{ct}$ of MAPbI$_3$:xRh ($x = 1\%$) reveals that a tiny amount of Rh-incorporated can enhance charge transport.
capacity. Therefore, supreme $J_{sc}$ is obtained from PSCs based on MAPbI$_3$:xRh ($x = 1\%$). Figure 4e presents steady-state photoluminescence (PL) spectrum of MAPbI$_3$:xRh/ SnO$_2$ films. Excitation wavelength is 465 nm. For MAPbI$_3$ films, a peak was around 780 nm. With the increase of Rh-incorporated content, the PL peak to appear slight blue shift. From Fig. 4e, the lower intensity of MAPbI$_3$:xRh (where $x = 0.5\%, 1\%$) film indicated extract electron carriers more effectively to SnO$_2$ electron transport layer, which is consistent with the larger FF.

The device measured in the forward and reverse scanning directions. Hysteresis characteristics of photocurrent are analyzed by the results of $J$–$V$ curves. Photocurrent hysteresis can be expressed by photocurrent hysteresis index (HI). The formula is (Eq. 1) [28]:

$$HI = \frac{PCE_{\text{reverse}} - PCE_{\text{forward}}}{PCE_{\text{reverse}}}$$ (1)

The HI of PSCs fabricated by MAPbI$_3$:xRh ($x = 0, 1\%$) is 0.042 and 0.020. Previous reports have shown that photocurrent hysteresis of devices mainly came from trap-induced carrier prevention. Therefore, lower photocurrent hysteresis indexes of devices fabricated by MAPbI$_3$:xRh ($x = 1\%$) suggest that higher trap-induced carrier prevention is taken.

The time-resolved PL spectrums of MAPbI$_3$:xRh films are shown in Fig. 4f. Usually, $\tau_1$ is attributed to bimolecular recombination of photogenerated carriers, while $\tau_2$ is due to trap-assisted recombination. Table S4 shows the details of parameters of carrier lifetimes. The decay time of pristine perovskite is $\tau_1 = 67$ ns and $\tau_2 = 693$ ns. The decay time of MAPbI$_3$:xRh ($x = 1\%$) is $\tau_1 = 63$ ns and $\tau_2 = 818$ ns. The passivation of rhodium ion mainly reduces grain boundaries and defects and increases carrier lifetime. To find the difference in average carrier lifetime ($\tau_{avg}$), the formula was defined as follows (Eq. 2) [42]:

$$\tau_{avg} = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i}$$ (2)

The $\tau_{avg}$ of pristine MAPbI$_3$ film is only 671 ns. MAPbI$_3$:xRh (where $x = 0.5\%, 1\%$) films possess longer $\tau_{avg}$, which is 726 and 796 ns. Because there is no charge transport layer, non-radiative recombination is the main reason for decay lifetime. Rh$^{3+}$ incorporation has long lifetime, which is reduced recombination and improve photocurrent of PSCs.

Space charge limited current (SCLC) was measured to study the mobility and defects density of perovskite films. Figure S7 shows device structures of the hole-only diode and the electron-only diode are shown. For electron-only device, SnO$_2$ and PCBM layer are used as the electron transport (blocking holes) layer being coated on both sides of the perovskite. For the hole-only device, the NiO and Spiro-MeOTAD layer is utilized as hole transport (blocking electrons) layer being coated on both sides of the perovskite. The current versus voltage ($I$–$V$) was tested under dark conditions by a Keithley model 2400. Three regions were evident in the experimental data. $I$–$V$ characteristics show three different regions: a linear ohmic region at low voltage (represented by the blue line); a trap-filling region from medium voltage to the trap-filled limit voltage ($V_{TFL}$) (represented by the orange line); a Child’s region (represented by the green line). The formula for trap density is [28]:

$$n_t = \frac{2\varepsilon\epsilon_0 V_{TFL}}{eL^2}$$ (3)

(where $V$ is the relative dielectric constant of perovskite hybrid materials, $\varepsilon_0$ is vacuum permittivity, $L$ is the thickness of perovskite layer). The charge carrier mobility ($\mu$) is estimated at the quadratic dependence region. The Mott–Gurney’s law is (Eq. 4) [28]:

$$I_d = \frac{9\varepsilon_0 \mu V^2}{8L^3}$$ (4)

(where $I_d$ is dark current density, and $V$ is the applied voltage). The trap-filling process for the hole-only device set is at $V_{TFL} = 0.33$ V for MAPbI$_3$ and $V_{TFL} = 0.14$ V for MAPbI$_3$:xRh (where $x = 1\%$); the trap-filling process for the electron-only device set is at $V_{TFL} = 1.12$ V for MAPbI$_3$ and $V_{TFL} = 0.57$ V for MAPbI$_3$:xRh (where $x = 1\%$). As shown in Table S10, the hole trap density of 1% Rh$^{3+}$-incorporated is $3.10 \times 10^{15}$ cm$^{-3}$ lower than MAPbI$_3$ (8.09 $\times 10^{15}$ cm$^{-3}$). The hole mobility of MAPbI$_3$:xRh (where $x = 0, 1\%$) is $1.29 \times 10^{-3}$ and $2.51 \times 10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$. Similarly, the electron trap density of 1% Rh$^{3+}$-incorporated is $1.26 \times 10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$. The decrease of trap densities of MAPbI$_3$:xRh (where $x = 1\%$) leads to both electron and hole mobility increase. We also measured $I$–$V$ curves of perovskite-only device by MAPbI$_3$:xRh (where $x = 0, 0.5\%, 1\%$ and 5%). Because the trap density is proportional to $V_{TFL}$, the trap density of MAPbI$_3$:xRh (where $x = 1\%$) is minimum (Fig. 4i). In polycrystalline perovskite films, there are many defects such as vacancies, dislocations and bond deformation because of the confusion of atomic arrangement on grain boundaries. Defects are mainly distributed on the gain boundaries [43]. The results of defect
density show that rhodium ion incorporation mainly plays the role of passivation grain boundary.

XRD patterns of MAPbI$_3$ and 1% Rh-incorporated perovskite films are exposed in the humid air before and after two months (Fig. 5). The aging rate of perovskite films is related to PbI$_2$ separated. Peak value of PbI$_2$ is higher, and perovskite film aging is faster. From Fig. 5b, the perovskite films based on MAPbI$_3$:xRh (where $x = 0.5\%$ and 1%) aged slower than that based on MAPbI$_3$ films. The addition of Rh$^{3+}$ made the perovskite structure more stable once again. The perovskite film stability directly affects the PSCs stability. The PSCs were stored in dry atmosphere without encapsulation for 500 h (Fig. 5c). Figure 5c shows that PSCs based on MAPbI$_3$:xRh (where $x = 1\%$) possess higher stability than that of MAPbI$_3$, maintained 92% of initial PCE after 500 h. Detail performance of PSCs is fabricated by MAPbI$_3$ and MAPbI$_3$:xRh with different aged time at dry air (Fig. S11 and Table S12).

4 Conclusion

Herein, Rh$^{3+}$ incorporation with tiny amount can help nucleation of perovskite grain, passivate grain boundary defects and improve properties of PSCs. In addition, Rh$^{3+}$ incorporation with perovskite can contribute to preparing larger crystalline and uniform film, reducing trap-state density and enlarging charge carrier lifetime. Therefore, planar heterojunction PSCs by MAPbI$_3$:xRh$^{3+}$ perovskite materials possess PCE of 20.71% without obvious photocurrent hysteresis. Meanwhile, the devices of Rh$^{3+}$-incorporated have high stability within 500 h without encapsulation in dry air. This work highlights the advantages of Rh$^{3+}$ incorporation in the capabilities of PSCs, which will promote the future industrial application.

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