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Cation-Exchange Approach for Fabrication of Efficient Methylammonium Tin Iodide Perovskite Solar Cells

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Abstract: Tin-based halide perovskite materials have been successfully employed in lead-free perovskite solar cells, but the overall power conversion efficiencies (PCEs) have been limited by the high carrier concentration from the facile oxidation of Sn^{2+} to Sn^{4+} . In view of the issue, herein a novel chemical route is developed for fabrication of high-quality methylammonium tin iodide perovskite (MASnl₃) films: hydrazinium tin iodide (HASnl₃) perovskite film is first solution deposited using presursors hydrazinium iodide (HAI) and tin iodide (Snl₂), and then transformed into MASnl₃ via a cation displacement approach. With the two-step process, a dense and uniform MASnI₃ film is obtained with large grain sizes and high crystallization. Moreover, the detrimental oxidation can be effectively suppressed by the hydrazine released from the film during the transformation. With the MASnl₃ as light harvester, mesoporous perovskite solar cells are prepared, and a maximum power conversion efficiency (PCE) of 7.13% is delivered with good reproducibility. The method provides new opportunities for the fabrication of low-cost and lead-free tin-based halide perovskite solar cells.

Hybrid organic-inorganic halide perovskite solar cells have attracted great attention because of their high energy conversion efficiency and relatively low processing cost. Since the first efficient device with a power conversion efficiency (PCE) of 9.7% reported in 2012, rapid progress has been made with the PCEs more than 23%.^{1,2} However, the high PCE values are only obtained in the lead-based perovskite devices, and the toxicity of lead and its compounds sheds doubt on their future large-scale deployment. Among the lead-free halide perovskites, tin-based perovskite materials hold particularly promising potential as light absorbers for solar cells, in view of their less toxicity, slightly narrower bandgaps (~ 1.3 eV) and greater charge mobility as compared with their lead counterparts.³⁻⁶ Despite of these excellent optical and electrical properties, the tin-perovskite solar cells have not achieved the deserved efficiencies, mainly due to severe bulk recombination from the facile oxidation of Sn²⁺ to Sn⁴⁺ in the perovskite films.⁷⁻⁹ In addition, the solution-processed tin perovskite materials usually suffer from low surface coverage

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due to uncontrollable crystallization in the film formation, leading to low device performance and poor reproducibility.⁷

In the past years, great efforts have been devoted towards improving the morphology of the tin perovskite films by solvent engineering and/or with various additives during the film fabrication.¹⁰⁻²³ For example, Hao et al. reported that the crystallization of the MASnI₃ perovskite films could be greatly improved through the solvated intermediate Snl₂·3DMSO,¹⁰ while Liao et al. demonstrated the formation of a dense and uniform FASnI₃ perovskite film through the use of mixed solvents and the antisolvent dripping.¹¹ Lately, Seok and co-workers used pyrazine to form a complex with SnF₂ to slow down the film crystallization, and achieved a PCE of 4.8%.¹² In addition, various organic cations have been reported to play an important role in improving the formation of the tin perovskite films and retarding the oxidation of Sn²⁺ to Sn^{4+, 13-22} Currently, SnF₂ has been extensively employed as an effective additive in the tin perovskite solar cells to reduce the background carrier density. An excessive amount of SnF2, however, deteriorates the perovskite film morphology and the device performance.13-24 Recently, Kanatzidis' group reported that reducing hydrazine vapor created in the spin coater could suppress the oxidation of Sn²⁺ during the film formation.^{25,26} In addition, reducing agents such as hypophosphorous acid (HPA) and hydrazinium chloride (N_2H_5CI) were employed as additives in the formation of the tin perovskite films.^{27,28} Despite of the great efforts involved and the progresses made, it is necessary to develop new and more effective strategies to further reduce the background carrier density and improve the performance of the tin perovskite solar cells.

In this work, a cation displacement approach is developed with a two-step process for the deposition of dense and uniform MASnl₃ perovskite layers with a low background carrier density. Firstly, a hydrazinium tin iodide (N₂H₅Snl₃, HASnl₃) layer was deposited by a simple solution technique. Then, the HASnl₃ film was in situ transformed into MASnl₃ in methylamine (CH₃NH₂ or MA) atmosphere through an organic cation displacement approach.^{29,30} With the route, a smooth and dense MASnl₃ film formed with large micron-sized grains and high crystallization. Moreover, the undesirable oxidation of Sn²⁺ to Sn⁴⁺ could be effectively suppressed by the reducing agent hydrazine generated inside the film during the cation displacement reaction. With the film as a light absorber, mesoporous heterojunction solar cells were fabricated with a maximum power conversion efficiency of 7.13%.

The HASnl₃ crystals were synthesized from a stoichiometric reaction between hydrazinium iodide (N₂H₅I) and Snl₂ in ethanol. The as-synthesized crystals show a needle-shaped structure with pale yellow color (shown in Figure S1). Different from 3D structural MASnl₃, the HASnl₃ presents an interesting 1D chain organic-inorganic hybrid structure, which is composed of 1D chain [Snl₃]_nⁿ⁻ anions and mono-protonated hydrazine H₂NNH₃⁺ cations, as shown in Figure 1. The Sn²⁺ ion in HASnl₃ is coordinated by five I⁻ anions, displaying a square pyramid

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Figure 1. (a) The one-dimensional $[Snl_3]_n^{n^-}$ anion chain structure in HASnl₃. (b) The packing diagram of HASnl₃, viewed down the *c*-axis. (c) Free energy profile for the chemical conversion of $CH_3NH_2 + NH_2NH_3^+ \rightarrow CH_3NH_3^+ + N_2H_4$. Energies are relative to substrate methylamine + hydrazine cation and are mass balanced.

configuration, the base of which consists of four μ_2 -I bridging atoms (I1 and I3), and the apex of which is occupied by an I terminal atom (I2). The Sn atoms are connected with each other by bridging I atoms, generating a one-dimensional (1D) anion chain $[Snl_3]_n^n$ along the *a*-axis (Figure 1a). Interestingly, the $[Snl_3]_n^n$ anion chains in HASnI₃ always appear back to back in pairs, with a short contact distance of 3.512 Å between the I3 atom in one $[Snl_3]_n^n$ anion chain and the nearest Sn atom in the other $[Snl_3]_n^n$ anion chain (Figure 1b). The charge-balanced $H_2NNH_3^+$ cations are located in the gap between the $[Snl_3]_n^n^$ anion chain pair. An N-H···I hydrogen bond exists between the terminal I atom and the mono-protonated N atom with the H···I distance of 3.478 Å, helping to stabilize the total crystal structure. Structural details can be found in the Supporting Information.

The HASnI₃ film was deposited on a mesoporous TiO₂ substrate by spin coating of the HASnI₃ solution in N,N-dimethylformamide, followed by drying at 80 °C for 5 min. The HASnI₃ film was then converted to MASnI₃ at 100 °C for 5 min in a closed vessel with MA gas. The conversion was carried out in a N₂-filled glove box. The experimental setup is shown in Figure S2. The conversion from HASnI₃ to MASnI₃ is rapid with the film color change from pale yellow to black upon exposing the film in the MA atmosphere. No liquid intermediate phase was observed during the conversion process, similar to those reported

previously.^{29,30} The conversion was proceeded through an in situ organic cation exchange reaction.

$$NH_2NH_3SnI_3$$
 (s) + CH_3NH_2 (g) $\rightarrow CH_3NH_3SnI_3$ (s) + NH_2NH_2 (g)

In the process, the MA molecules diffuse inside the HASnI₃ film, and interact with NH₂NH₃⁺ to form the complex (Int1), followed by the chemical conversion of CH₃NH₂ + NH₂NH₃⁺ \rightarrow CH₃NH₃⁺ + N₂H₄ via a transition state of NH₂NH₂··H··CH₃NH₂. This process is highly kinetically favorable by the free energy change (Δ G) of -0.93 eV. Finally, the generated N₂H₄ gas is released from the surface of MASnI₃ by crossing a barrier (0.53 eV relative to Int2) under the reaction conditions of 100 °C. The free energy profile for the chemical conversion is presented in Figure 1c. With the cation exchange, the pristine HASnI₃ with 1D [SnI₃]_nⁿ⁻ chains are reconstructed to form stable 3D MASnI₃ perovskite.



Figure 2. UV-Vis absorption spectra (a) and X-ray diffraction patterns (XRD) (b) of the HASnI₃ and resultant MASnI₃ films. Scanning electron microscopy (SEM) images of the HASnI₃ (c) and resultant MASnI₃ (d) films on mesoporous TiO_2 substrates.

UV/vis spectra and XRD patterns were recorded for the HASnI₃ and the resultant MASnI₃ films. As shown in Figure 2a, the absorption edge is significantly extended to ~ 950 nm with enhanced optical absorption in the entire spectral range after the conversion for 5 min. This is in agreement with the color change observed, confirming the formation of MASnI₃. Different from the XRD patterns of the ground HASnI₃ powders (Figure S3), only few of the peaks appeared for the deposited film, as shown in Figure 2b, indicating the anisotropic properties of the formed HASnl₃ film. The XRD patterns of the MASnl₃ film presents the characteristic peaks corresponding to the tetragonal phase of MASnl₃.⁷ It is interesting to note that the MASnl₃ film converted from the HASnl₃ shows stronger optical absorption and higher diffraction peak intensity, as compared with those from the conventional one-step MASnI₃ film (Figure S4). In addition, the complete conversion of HASnl₃ to MASnl₃ was further confirmed by ¹H nuclear magnetic resonance (NMR) spectra shown in Figure S5.

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surface The microstructure and morphology were characterized for the HASnI₃ film before and after the conversion by scanning electron microscopy (SEM). As can be seen in Figure 2c, the pristine HASnl₃ film displayed a morphology of worm-like aggregates, which are orderly and densely aligned on the substrate, reflecting its 1D structural characteristics. The morphology was changed strikingly after the conversion, from the bound rods to compact and homogeneous granular grains with sizes of ~ 1 μ m (Figure 2d). The structure is highly desirable for photovoltaic devices due to the minimized grain boundary energy for charge transfer to the electron- and hole-collecting layers. It should be noted that the pinhole-free and compact HASnI₃ film is a prerequisite for the formation of a dense and continuous MASnl₃ film by the in-situ solid-gas reaction. As expected, the MASnl₃ film from the one-step process exhibited a much rough surface with clear phase segregation and many pinholes due to fast crystallization between the precursors Snl₂ and MAI (Figure S6).



Figure 3. (a) Device architecture of a typical mesoporous perovskite solar cell (FTO glass/compact TiO₂ layer/mesoporous TiO₂ layer/MASnl₃/PTAA/Au). (b) J–V curves of the studied devices based on the one-step or the two-step MASnl₃ layer. (c) Incident photon-to-current efficiency (IPCE) spectrum for the perovskite device with the two-step MASnl₃ layer. (d) PCE histogram for 60 solar cells with the two-step MASnl₃ layer.

After the demonstration of the high-quality MASnI₃ perovskite films prepared by the two-step process, mesoporous perovskite solar cells were prepared with a structure of FTO/compact TiO₂/mp-TiO₂/MASnI₃/PTAA/Au, as shown in Figure 3a for the cross-sectional SEM image of a complete device. For comparison, the one-step MASnI₃ film was employed in the devices with the same structure. The detailed information of the device fabrication is described in the Experimental Part. The photovoltaic metrics of the devices were evaluated by measuring their photocurrent density versus voltage (J-V) curves and their incident photon-to-current conversion efficiency (IPCE). The best J-V curves of the devices were illustrated in Figure 3b, recorded by reverse scan with 10 mV voltage steps and 10 ms delay times under AM 1.5 G illumination. The corresponding photovoltaic parameters, including open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), and fill factor (FF) were listed in the inset of Figure 3b. For the device with the one-step MASnl₃ layer, a PCE of 0.11% ($J_{sc} = 2.62 \text{ mA/cm}^2$, $V_{oc} = 0.156 \text{ V}$, and FF = 0.27) was given, which is in consistent with the previous reports.^{10,12} It is believed that the low performance can originate from the poor quality of the MASnl₃ layer with high background carrier density from the oxidation of Sn²⁺. In contrast, the PCE of the device with the two-step MASnl₃ layer was significantly improved to 7.13% with a J_{sc} of 22.91 mA cm², a V_{oc} of 0.486 V, and a FF of 0.64, which is among the best values reported for the MASnl₃-based solar cells so far.^{22,25} All the improved photovoltaic parameters can be due to the formation of good quality MASnl₃ film with a low background carrier density.

Figure 3c shows the IPCE spectrum for the device with the two-step MASnl₃ layer, displaying a high average value in the 350- to 950-nm wavelength range, well consistent with the absorption profile of the corresponding MASnl₃ film. The integrated J_{sc} calculated from the IPCE is about 22.62 mA cm⁻², very close to the J_{sc} obtained from the *J*-V curve. The PCE histogram in Figure 3d presents an average PCE of 6.32 ± 0.46% for 60 solar cells. The statistical box plots of photovoltaic parameters for the devices with the one-step and two-step MASnl₃ layers were shown in Figure S7. To evaluate the stabilized power output of the devices, a typical device with the two-step MASnl₃ layer was measured at a maximum power voltage of 0.342 V, showing a steady-state PCE and current density of 6.83% and 19.97 mA cm⁻², respectively, as shown in Figure S8.

It is well known that the Sn²⁺ is easily oxidized into Sn⁴⁺ during the film fabrication, and the excess Sn⁴⁺ can cause the self-doping of the tin perovskite and deteriorate the performance of the device. To elucidate the enhanced photovoltaic performance



Figure 4. Top: XPS Sn 3d spectra of the one-step (a) and two-step (b) MASnI₃ films, recorded before and after the etching (30 s). Measured results, black line; Sn²⁺ state, red line; Sn⁴⁺ state, blue line; background, gray line; sum of all deconvolution curves, green line. Bottom: Steady state (c) and time-resolved (d) PL spectroscopy of the MASnI₃ films.

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of the devices with the two-step MASnl₃ layer, the Sn states were analyzed and compared by XPS for both the MASnI₃ films prepared from the one-step and two-step processes. For differentiating the oxidation on surface and in the interior, the films were etched with Ar⁺ sputtering for 30 s for the detection of the bulk of MASnI₃ films. As shown in Figure 4a, b, and Table S1, the pristine one-step MASnI₃ film presents two broad peaks at 495.7 and at 487.4 eV for Sn 3d_{3/2} and Sn 3d_{5/2}, respectively, each displaying a distinct shoulder at lower energy due to the co-existence of Sn4+ and Sn2+ species. The amount of Sn4+ species was found to be about 86.2%, indicating serious oxidation of Sn²⁺ on the surface, even if SnF₂ is present in the layer. In contrast, the proportions of Sn⁴⁺ species are only 17.3% on the surface for the two-step MASnI₃ film. After the etching, the amount of Sn⁴⁺ is decreased to 64.6% for the one-step MASnI₃ film, which is still high, and similar to the previous reports.12

On the contrary, the content of Sn⁴⁺ is only 4.8% in the twostep MASnl₃ film after the etching. The results indicate that the oxidization of Sn²⁺ to Sn⁴⁺ was significantly suppressed from the surface to the inferior in the two-step MASnl₃ film. As compared with the previous report,^{25,26} where the tin perovskite films were fabricated under hydrazine atmosphere introduced from outside, the method reported here provide a more effective approach for retarding the oxidation because the hydrazine is generated inside the film and can efficiently reduce Sn⁴⁺ species in situ as $2Snl_6^{2-} + N_2H_4 \rightarrow 2Snl_4^{2-} + N_2 + 4Hl_{-}^{25}$ Additionally, unfavorable zero-valent tin was not detected from the spectra, implying that the over reduction of Sn⁴⁺ by the hydrazine can be averted in the cation displacement.

In order to gain deep insight into the charge dynamics in the MASnI₃ films steady-state and time-resolved photoluminescence (PL) spectroscopy were performed, as shown in Figure 4c and d. Both the MASnI₃ films presented the steady-state PL spectra with peaks at around 980 nm, while the two-step film shows higher PL intensity as compared to the one-step film, indicating suppression of nonradiative recombination due to the reduced grain boundary and low carrier concentration observed above. Figure 4d shows the time-resolved PL spectra, where the twostep MASnI₃ film showed relatively longer PL lifetime (T = 3.51 ns) as compared to the one-step counterpart (T = 0.88 ns), measured by assuming a first-order decay (single-exponential decay). This increase of the PL lifetime further confirms a marked reduction of charge recombination in the MASnI₃ film due to the effective suppression of Sn^{2+} oxidation by the hydrazine generated inside the film during the transformation.

In summary, we report a simple cation-displacement approach to make high quality MASnl₃ films to afford high-efficiency Snperovskite solar cells. High-quality, pinhole-free MASnl₃ films are achieved after the conversion from the pristine HASnl₃ perovskite films. Moreover, the oxidation of Sn²⁺ to Sn⁴⁺ can be efficiently suppressed due to the reduction agent hydrazine generated inside the film in the conversion. Both the results are particularly necessary for high efficiency tin perovskite solar cells. With the MASnl₃ film as light absorber, the mesoporous MASnl₃ perovskite solar cells were fabricated with high reproducibility, exhibiting a maximum PCE of 7.13% with average PCEs of 6.32% ± 0.46%. This work provides a new and effective strategy for the fabrication of high efficiency tin perovskite solar cells. We anticipate that, the performance of the tin perovskite solar cells would be improved with further optimization of the structure design and interface engineering.

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Keywords: lead-free perovskites • solar cells • thin films • cation displacement

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High-quality, pinhole-free CH₃NH₃SnI₃ films are achieved from the pristine NH₂NH₃SnI₃ perovskite, and the oxidation of Sn²⁺ to Sn⁴⁺ can be efficiently suppressed due to the reduction agent hydrazine generated inside the films in the conversion. With the CH₃NH₃SnI₃ film as light absorber, the mesoporous MASnI₃ perovskite solar cells were fabricated, exhibiting a maximum PCE of 7.13%.



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