Efficient Ag-Doped Perovskite Solar Cells Fabricated in Ambient Air

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Abstract: So far, it is still a great challenge to prepare high efficiency organic–inorganic perovskite solar cells in ambient air. Specifically, moisture is easily combined with the perovskite material during the spin-coating process, which result in porous perovskite films with poor surface morphology. In this study, we investigated crystalline Ag-doped perovskite films by a one-step spin-coating method in air with 30–40% relative humidity (RH), in which ethyl acetate (EA) was used as antisolvent can absorb moisture in air to reduced nucleation density. More significantly, EA is a feasible and environmentally friendly solvent to replace highly toxic solvent. Moreover, 1.0% Ag-doped device shows a highest power conversion efficiency (PCE) of 14.36%. The improved performance is not only ascribed to the superior CH$_3$NH$_3$PbI$_3$ film with high crystallinity but to the versatile tunability of energy band structure.

Keywords: perovskite solar cells; Ag-doped; 30–40% RH; ethyl acetate (EA)

1. Introduction

Recently, worldwide efforts have been made to continuously improve the power conversion efficiency (PCE) of perovskite solar cells (PSCs) [1]. High performance of PSCs can be attributed to excellent photoelectric property of high absorption coefficient, tunable band gap, and long charge carrier diffusion length [2–4]. CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$) is a typical perovskite material in which the electronic band structure is mainly determined by the Pb and I and the monovalent cation MA$^+$ which mainly regulates the lattice constants of perovskite crystals [5,6]. It is inevitable that the composition of perovskite would affect optoelectronic properties including the light absorption, carrier transport property and the band gap. It has shown that tuning the energy band structure and properties of perovskite materials through a partial substitution of the divalent metal, such as Sn, Ca, or Ba [7–9], the monovalent cation (e.g., K, Na, Cu) or trivalent cation such as Bi or In for Pb [10–13]. However, in the cationic doping behavior of MAPbI$_3$, there are few reports of Ag-doped perovskite [14,15]. It has been found that Ag-doped perovskite material MAPb$_{1-x}$Ag$_x$I$_3$ has a p-type conductive behavior by using the first-principles calculations [16].

Despite numerous studies for high efficiency of PSCs, the fabrication process of the perovskite layer and devices storage conditions is very sensitive to moisture, oxygen, and another environmental factor. So far, most of the research on high efficiency perovskite devices was obtained under the relatively low oxygen and moisture in gloveboxes [17–20]. In fact, it needs to be solved that the fabrication and storage of perovskite solar cells in air for further commercial production and application. Therefore, researchers have been trying to fabricate perovskite films and devices in ambient air. Tan et al. reported a simplified close space sublimation (CSS) deposition to grow a high quality MAPbI$_3$ thin film in a...
low-vacuum and even non-vacuum oven [21]. Yu et al. found the modest crystal growth under high humid condition of 70% RH can benefit the formation of perovskite films with high crystallinity and low crystal defect density [22]. Recently, the green solvents of ethyl acetate (EA) or methyl acetate (MA) was employed as antisolvent during one-step deposition in air to fabricate perovskite solar cells [23,24]. Singh et al. demonstrated that EA was used as an antisolvent to obtain the mixed cation Cs/MA/FA perovskite film with high crystallinity and the perovskite device with high efficiency of 19.8% [23].

So far, it is difficult to synthesize high-efficiency perovskite batteries in the air by simple and feasible methods. There is no research report on the synthesis of Ag-doped perovskite in air. Therefore, both performance improvement of devices and environmentally friendly considerations, Ag was attempted to partially substitute toxic Pb in MAPbI$_3$ perovskite films. In this work, Ag$^+$ was chosen as the doping element to partially replace Pb$^{2+}$ due to their similar ionic radii, which could improve the film morphology and crystallinity. In addition, Ag incorporation has a potential impact on tuning energy band structures of organic–inorganic perovskite materials. The green antisolvent EA was used to replace highly toxic, common solvent chlorobenzene (CB) or toluene (TL). Therefore, the Ag-doped MAPbI$_3$ perovskite films were formed in ambient air with 30–40% relative humidity (RH).

When the Ag$^+$ doping content is 1.0%, the perovskite film with higher crystallinity and full surface coverage was obtained. It is found that the Fermi energy level of Ag-doped MAPbI$_3$ material slight downshift towards the valence band edge, which improve the charge carrier transport. As a result, the Ag-doped PSCs fabricated in ambient atmosphere with a power conversion efficiency (PCE) of 14.26% is observed. We believe that this study would provide a good direction for PSCs development in ambient air.

2. Materials and Methods

2.1. Materials

The transparent conductive FTO/glass substrates with sheet resistance of 10 Ω/sq was purchased from Pilkington glasses. The titanium(IV) isopropoxide (99.5%) was supplied by Alfa Aesar Chemical Co., Ltd.(Shanghai, China); Lead(II) iodide (PbI$_2$, 99%) was proved by Sigma-Aldrich Co. (Shanghai, China); Silver iodide (AgI, 99.99%), N,N-Dimethylformamide (DMF, 99.9%) and chlorobenzene (99.5%) were purchased from Aladdin Ltd. Co. All the other materials were obtained from Xi’an Polymer Light Technology Crop., including Methylammonium iodide (MAI, 99.5%), Spiro-OMeTAD (99.5%), Li-TFSI (99%) and TBP (96%).

2.2. Device Fabrication

FTO/glass substrates were cleaned in acetone, isopropanol and ethanol, deionized water sequentially for 15 min and then dried under air stream. The synthesis process of the Ag-doped perovskite solar cells can refer to the reported method [25]. The compact TiO$_2$ layer was prepared by spin-coating the precursor consisting of 100 µL titanium (IV) isopropoxide, 2.5 mL ethanol and 20 µL dilute hydrochloric acid at 3000 rpm/30 s and subsequently sintering at 500 °C for 30 min. The substrates were further treated with 40 mM TiCl$_4$ aqueous solution at 70 °C for 30 min in the oven, and then cleaned with deionized water to sinter at 500 °C for 30 min. The mesoporous TiO$_2$ layer was obtained by spin-coating the precursor consisting of a TiO$_2$ paste diluted by ethanol of 1:7 weight ratio at 4500 rpm/40 s and then baked at 500 °C for 30 min. After cooling to room temperature, the TiO$_2$ films were immersed into 20 mM TiCl$_4$ solution at 70 °C for 30 min and then heated treated at 500 °C for 30 min. To obtain the Ag-doped perovskite materials, the AgI, CH$_3$NH$_3$I and PbI$_2$ with a molar ratio of x:1:−x (0 ≤ x ≤ 0.05) were dissolved in DMF to prepare Ag-doped perovskite precursor solution whose concentration were 0%, 0.5%, 1.0%, 3.0%, and 5.0%, respectively. The perovskite layer was obtained by one step solution technique in ambient air with 30–40% RH, in which the precursor solution was spin-coated onto the mesoporous TiO$_2$ layer at 4000 rpm for 20 s. During the spin-coating process, 100 µL EA antisolvent was dripped onto the precursor film after about
6 s, and then annealed at 100 °C. The hole transport material consisting of 72.3 mg spiro-
OMeTAD in 1 mL chlorobenzene with additives consisting of 17.5 µL Li-TFSI/acetonitrile
(520 mg/mL), 28.8 µL of TBP was spin-coated at 2000 rpm for 40 s. Ag electrode with
100 nm was deposited on the top of the device using thermal evaporation. Finally, the
Ag-doped perovskite solar cells were successfully obtained. The active area was 0.1 cm².

2.3. Characterization Techniques

X-ray diffraction (XRD) test were carried out by an X-ray power diffractometer (D8
Advance, Bruckers AXS, Cu Ka radiation). The morphological properties of the samples
were characterized by the S-4800 scanning electron microscope (SEM). X-ray photoelectron
spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) were carried out by
ESCALAB 250Xi (ThermoFisher Scientific). Photocurrent density–voltage (J–V) curves of
solar cells were measured with a Keithley 2400 source meter under the simulated AM 1.5G
illumination at a calibrated intensity of 100 mW/cm² by a Class AAA solar simulator at
room temperature in the air, and the scanning direction is from open circuit at 1.2 V to
short circuit at 0 V with a scan rate of 100 mV/s. Steady-state photo-luminescence (PL)
spectroscopy was measured with an excitation wavelength of 510 nm. The light absorption
spectra were recorded on a UV-vis-NIR spectrophotometer (Cary 5000).

3. Results and Discussion

Here, Ag⁺ is chosen to partially substitute Pb²⁺ because its ionic radius of 12.9 Å is
close to that of Pb²⁺ (13.3 Å) to tune the electrical properties and energy band structure
of MAPbI₃ perovskite material [15]. XRD patterns of perovskite films with Ag-doped
concentration from 0% (pristine) to 5.0% are shown in Figure 1. The three strong scattering
peaks located at 20 values of 14.20°, 28.51°, and 31.92° can be identified with reflections
form (110), (220), and (310) planes, suggesting that the MAPbI₃ films with tetragonal crystal
structure were obtained in this study. In addition, an increase in diffraction intensity
of Ag-doped MAPbI₃ materials can be observed in the patterns. Specially, significant
changes manifested in full width of half maximum (FWHM) of the strongest (110) diffraction peaks,
in which the FWHM value of 1.0% Ag concentration is 0.105 lower than that of pristine
sample (0.124). The results indicate that the crystallinity is enhanced by appropriate Ag
doping amount.

![Figure 1. XRD patterns of Ag-doped perovskite films in which Ag incorporation is 0%, 0.5%, 1.0%,
3.0%, and 5.0%.](image-url)

The SEM images of perovskite films is shown in Figure 2a–e. It is found that the
roughness of Ag-doped MAPbI₃ thin films obtained in air is slightly higher, which may be
ascribed to the grain-merging tendency induced by humidity annealing conditions [26,27].
We calculated the grain size of Ag-doped MAPbI\textsubscript{3} materials and displayed the distribution statistically in Figure S1 according to the SEM images. It shows the grain size centrally of Ag-doped MAPbI\textsubscript{3} thin films distributes at 200 nm that is larger than that of pristine sample. The 1.0\% Ag-doped MAPbI\textsubscript{3} thin film exhibits a uniform surface morphology and high crystalline quality, which occurs possibly because EA can absorb the water in air rather than reacted with precursor solution. Therefore, the reduced nucleation density makes it possible for more solute to merge with formed nucleus to generate bigger grains in air with high humidity.

![Figure 2. Top-view SEM images of perovskite films with different Ag incorporation: (a) 0\%, (b) 0.5\%, (c) 1.0\%, (d) 3.0\%, and (e) 5.0\%.](image)

In order to study the effect of Ag doping on the optical properties of MAPbI\textsubscript{3} films, the UV-visible absorption spectral of perovskite thin films shown in Figure 3a. All samples have similar absorption curves in the range from 400 nm to 800 nm. The absorption intensity of Ag-doped MAPbI\textsubscript{3} samples is obviously stronger than that of undoped sample between 400 nm to 550 nm, suggesting that Ag incorporation increases light harvesting capability. Meanwhile, the Tauc plots was inserted in the UV-IR spectra to estimate the band gap of all samples, in which the band gap of samples with 0, 0.5\%, 1.0\%, 3.0\%, and 5.0\% Ag doping concentration is 1.588, 1.601, 1.596, 1.588, and 1.589 eV, respectively. This indicates the band gap of perovskite materials increased a little than that of pristine MAPbI\textsubscript{3} material. Furthermore, the steady-state PL spectra of perovskite films deposited on the hole transport layer are displayed in Figure 3b. It shows all PL peaks can be observed at around 766 nm. It is found that the PL peak intensity of Ag-doped perovskite films/spiro-OMeTAD first decreases and then increases with the Ag-doped amount. In addition, the emission peaks of Ag-doped perovskite films with Ag corporation concentration of 0.5\% and 1.0\% have a slightly blue shifts, which is consistent with the results of the UV-visible absorption spectral. Another phenomenon can be addressed is that the intensity of the emission peak of 1.0\% Ag doping MAPbI\textsubscript{3} material was reduced sharply, suggesting that the better excitation separation at the Ag-doped MAPbI\textsubscript{3} layer/the hole transport layer interface [28], which would be improve the photovoltaic conversion performance of perovskite solar cells.
Considering the influence on the energy band structure of MAPbI$_3$ perovskite material after doping Ag$^+$, as well as the polarity, the ultraviolet photoelectron spectra (UPS) was used to characterize the change and the results are shown in Figure 4 and the Fermi energy level position has been calibrated. The valence band edge of 1.0% Ag-doped MAPbI$_3$ material is closer to the Fermi energy level position than that of pristine sample. The result indicates that Ag doping in perovskite film would lead to the polarity transition from the initial n-type character to a p-type character [29,30], which will enhance the charge transport property of photogenerated holes at the interface. In order to detect the chemical composition distribution and electronic structure of perovskite films, the X-ray spectroscopy (XPS) was carried out to obtain relative element information of Ag-doped MAPbI$_3$ materials prepared in air. The C, N, Pb, and I elements can be successfully observed in both similar XPS spectra shown in Figure S2a,b, indicating the formation of MAPbI$_3$ films. In the high-resolution XPS spectrum, the presence of the Ag 3d$^{5/2}$ and Ag 3d$^{3/2}$ can be confirmed in the Ag-doped perovskite film.

To assess the influence of Ag doping behavior on the trap states of perovskite materials, we fabricated capacitor-like devices of FTO/perovskite with different Ag doping concentration/Au based on space-charge-limited current (SCLC) method to evaluate the trap density shown in Figure 5. The I-V curves plotted on a double log were acquired in the dark, which can be divided into two parts: the ohmic region where the current increased linearly with increasing voltage in the low bias voltage, and the trap-filled limit region where current increased nonlinearly in the high bias voltage [31,32]. To evaluate the
trap-state density \( (n_t) \) in the Ag-doped MAPbI\(_3\) samples, the trap filled limit voltage \( (V_{TFL}) \) is the transition point from the ohmic region to the trap-filled limit region, which can be obtained using the following equation [33,34]: This is example 1 of an equation:

\[
V_{TFL} = \frac{enKL^2}{2e\varepsilon_0}
\]

where \( e \) is the elementary charge of the electron, \( L \) represents the thickness of the perovskite films, \( \varepsilon \) is the relative dielectric constant of perovskite films and is the vacuum permittivity. The \( V_{TFL} \) values of devices with Ag corporation concentration from 0 to 5.0% were 0.874, 0.686, 0.691, 0.915, and 0.964 V. From the Equation (1), the trap-state density \( n_t \) of Ag-doped samples with 0, 0.5%, 1.0%, 3.0%, and 5.0% is calculated to be \( 2.52 \times 10^{16} \), \( 2.00 \times 10^{16} \), \( 2.64 \times 10^{16} \), \( 2.78 \times 10^{16} \) cm\(^{-3} \). It shows the perovskite films with 3.0% and 5.0% Ag doping have similar defect states to that of the undoped MAPbI\(_3\) sample. However, the 0.5% and 1.0% Ag doping can decrease the trap-state density of perovskite materials. Therefore, the appropriate Ag doping concentration can passivate the defect of MAPbI\(_3\) films, which improve the performance of perovskite solar cells.

![Figure 5. Current density–voltage characteristics of devices with FTO/perovskite/Au configuration utilized for estimating the defect density in perovskite films with Ag corporation concentration from 0 to 5.0%.

Figure 6 shows the photocurrent density-voltage (J-V) characteristic curves of perovskite solar cells based on the FTO/c-TiO\(_2\)/m-TiO\(_2\)/perovskite/Ag. It is found that the J-V performance of Ag-doped perovskite solar cells first increases and then decreases with the Ag-doped amount. The undoped perovskite device has a power conversion efficiency (PCE) of 11.40% with an open circuit voltage (\( V_{OC} \)) of 0.973 V, a short-circuit current density (\( J_{SC} \)) of 21.08 mA/cm\(^2\) and a fill factor (FF) of 0.556. On the contrary, the 1.0% Ag-doped perovskite device exhibited a highest PCE of 14.26% with a \( V_{OC} \) of 1.035 V, a \( J_{SC} \) of 22.08 mA/cm\(^2\) and an FF of 0.624 in Table 1. Such high device performance should be ascribed to the compact and uniform perovskite film, the decrease in trap-state density and increase in charge extraction capacity of 1.0% Ag-doped perovskite device. When the Ag doping concentration increased to 3.0% and 5.0%, the PCE of devices decreased to 11.12% and 10.74%, which may be due to the carrier recombination in the bulk of perovskite film or at the perovskite layer/charge transport layer interface. In addition, good device repeatability of Ag-doped perovskite solar cells prepared in air with 30–40% RH can be shown in Figure S3. J-V hysteresis phenomenon is possibly to the polarization at the interface, motion of ions, the change of electronic properties between the contact
interfaces and ferroelectric effect. The 1.0% Ag-doped perovskite solar cell (RS-A) with a test of backward direction exhibited a highest PCE of 11.68% with a V\textsubscript{OC} of 0.976 V, a J\textsubscript{SC} of 19.88 mA/cm\textsuperscript{2} and an FF of 0.602 in Figure S4. The Ag-doped perovskite solar cell (FS-A) with a test of forward direction exhibited a highest PCE of 10.68% with a V\textsubscript{OC} of 0.935 V, a J\textsubscript{SC} of 19.87 mA/cm\textsuperscript{2} and an FF of 0.575 in Table S1. However, the pristine perovskite device shows a PCE (RS-P) of 9.10% and a PCE (FS-P) of 7.25%. Benefited from the tuned band structure and reduced surface defect, the V\textsubscript{OC} was improved from 0.935 to 0.976 V. The increasing of FF mainly was ascribed to less recombination in the Ag-doped perovskite solar cell. Based on the stability evaluation, Ag-doped device exhibits stabilized power output performance within 300s under continuous maximum point tracking test shown in Figure S5.

![J-V curves of perovskite solar cells based on the FTO/c-TiO\textsubscript{2}/m-TiO\textsubscript{2}/perovskite/spiro-OMeTAD/Ag.](image)

**Figure 6.** J-V curves of perovskite solar cells based on the FTO/c-TiO\textsubscript{2}/m-TiO\textsubscript{2}/perovskite/spiro-OMeTAD/Ag.

**Table 1.** Photovoltaic performances summary of the perovskite devices.

| Ag Concentration | Voc (V) | Jsc (mA/cm\textsuperscript{2}) | FF   | PCE (%) |
|------------------|---------|-------------------------------|------|---------|
| 0%               | 0.973   | 21.08                         | 0.556| 11.40   |
| 0.5%             | 0.997   | 22.04                         | 0.608| 13.35   |
| 1.0%             | 1.035   | 22.08                         | 0.624| 14.26   |
| 3.0%             | 0.974   | 21.88                         | 0.522| 11.12   |
| 5.0%             | 0.994   | 21.13                         | 0.511| 10.74   |

4. Conclusions

In this study, Ag-doped perovskite films have been successfully prepared by one step deposition process in ambient air of 30–40% RH. We observed that the Ag-doped samples exhibit uniform surface morphology, indicating a higher crystalline quality, which possibly because EA can absorb the water in air rather than reacted with precursor solution. The 1.0% Ag-doped MAPbI\textsubscript{3} device has a higher power conversion efficiency of 14.36%, showing an improvement of 20.1% over that of the pristine device. Such an obvious performance enhancement arises not only from strongly increased charge transport efficiency but also from the lower trap state of perovskite material.

**Supplementary Materials:** The following are available online at [https://www.mdpi.com/article/10.3390/cryst11121521/s1](https://www.mdpi.com/article/10.3390/cryst11121521/s1), Figure S1: The statistical diagram of perovskite grain size with different Ag incorporation: (a) 0%, (b) 0.5%, (c) 1.0%, (d) 3.0% and (e) 5.0%; Figure S2. The XPS spectra of (a) pristine MAPbI\textsubscript{3} film and (b) 1.0% Ag-doped perovskite film, and the XPS for the elements C, N, Pb, Ag and I; Figure S3. The distribution diagram of perovskite devices with Ag doping concentration...
from 0 to 5.0% in air with 30%-40% RH, data from 20 pieces per variable condition; Figure S4. J-V curves of perovskite solar cells based on the FTO/c-TiO2/m-TiO2/perovskite/spiro-OMeTAD/Ag; Figure S5. Steady power conversion efficiency curve of the 1.0% Ag-doped perovskite solar cell; Table S1: Table S1. Photovoltaic performances summary of the perovskite devices.

Author Contributions: Conceptualization, J.H. and H.H.; methodology, J.H. and H.H.; investigation, Z.W. and B.P.; data curation, Z.W. and B.P.; writing—original draft preparation, J.H.; writing—review and editing, H.G. and Q.Q.; supervision, G.W. and J.W.; project administration, H.H.; funding acquisition, H.H. All authors have read and agreed to the published version of the manuscript.

Funding: This work is supported by the Fundamental Research Funds for the Central Universities under Grand No. 2652017154 and 2652017163, and the National Natural Science Foundation of China under Grand No. 11404293.

Data Availability Statement: Not applicable.

Acknowledgments: We wish to express our gratitude to the members of our research team, Jiabin Hao, Zeming Wang, Huying Hao, Guanlei Wang, Hongcheng Gao, Jianyu Wang, Bing Pan, Qiang Qi.

Conflicts of Interest: The authors declare no conflict of interest. We identify and declare any personal circumstances or interest that may be perceived as inappropriately influencing the representation or interpretation of reported research results. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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