Article

Efficient Ag-Doped Perovskite Solar Cells Fabricated in Ambient Air

Jiabin Hao ^{1,*}, Zeming Wang ², Huiying Hao ^{3,*}, Guanlei Wang ¹, Hongcheng Gao ¹, Jianyu Wang ¹, Bing Pan ¹ and Qiang Qi ¹

¹ Department of Chemical Engineering, Chengde Petroleum College, Chengde 067000, China; wangguanlei@126.com (G.W.); gaohc_85@163.com (H.G.); polymer168@126.com (J.W.); taode_JW@163.com (B.P.); qiqiang7911@163.com (Q.Q.)

² Hebei Tourism Vocational College, Chengde 067000, China; Wangzm_89@126.com

³ School of Science, China University of Geosciences, Beijing 100083, China

* Correspondence: jiajooy@163.com (J.H.); huiyinghaol@cugb.edu.cn (H.H.)

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 $\text{CH}_3\text{NH}_3\text{PbI}_3$ film with high crystallinity but to the versatile tunability of energy band structure.

Citation: Hao, J.; Wang, Z.; Hao, H.; Wang, G.; Gao, H.; Wang, J.; Pan, B.; Qi, Q. Efficient Ag-Doped Perovskite Solar Cells Fabricated in Ambient Air. *Crystals* **2021**, *11*, 1521. <https://doi.org/10.3390/cryst11121521>

Academic Editors: M. Ajmal Khan and Saripally Sudhaker Reddy

Received: 2 November 2021

Accepted: 1 December 2021

Published: 6 December 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

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]. $\text{CH}_3\text{NH}_3\text{PbI}_3$ (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 $\text{MAPb}_{1-x}\text{Ag}_x\text{I}_3$ 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 MAPbI₃ perovskite films. In this work, Ag⁺ was chosen as the doping element to partially replace Pb²⁺ 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 MAPbI₃ 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 MAPbI₃ 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 (PbI₂, 99%) was provided 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 TiO₂ 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 TiCl₄ 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 TiO₂ layer was obtained by spin-coating the precursor consisting of a TiO₂ 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 TiO₂ films were immersed into 20 mM TiCl₄ 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, CH₃NH₃I and PbI₂ with a molar ratio of x:1:1–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 TiO₂ 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 μ L Li-TFSI/acetonitrile (520 mg/mL), 28.8 μ L 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 2 θ values of 14.20°, 28.51°, and 31.92° can be identified with reflections from (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%.

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 MAPbI₃ materials and displayed the distribution statistically in Figure S1 according to the SEM images. It shows the grain size centrally of Ag-doped MAPbI₃ thin films distributes at 200 nm that is larger than that of pristine sample. The 1.0% Ag-doped MAPbI₃ 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%.

In order to study the effect of Ag doping on the optical properties of MAPbI₃ 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 MAPbI₃ 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 MAPbI₃ 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 MAPbI₃ material was reduced sharply, suggesting that the better excitation separation at the Ag-doped MAPbI₃ layer/the hole transport layer interface [28], which would be improve the photovoltaic conversion performance of perovskite solar cells.

Figure 3. (a). The UV-visible absorption spectral of Ag-doped perovskite films, the insert image is Tauc plot curves; (b) Steady-state PL spectra of Ag-doped perovskite films deposited on spiro-OMeTAD.

Considering the influence on the energy band structure of MAPbI₃ 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 MAPbI₃ 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 MAPbI₃ 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 MAPbI₃ 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.

Figure 4. The UPS spectra of pristine MAPbI₃ film and 1.0% 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 MAPbI₃ 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:

$$V_{TFL} = \frac{en_t L^2}{2\epsilon\epsilon_0} \quad (1)$$

where e is the elementary charge of the electron, L represents the thickness of the perovskite films, ϵ 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 2.52×10^{16} , 1.98×10^{16} , 2.00×10^{16} , 2.64×10^{16} , and $2.78 \times 10^{16} \text{ cm}^{-3}$. It shows the perovskite films with 3.0% and 5.0% Ag doping have similar defect states to that of the undoped MAPbI₃ 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 MAPbI₃ 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-TiO₂/m-TiO₂/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/cm² 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/cm² 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_{OC} of 0.976 V, a J_{SC} of 19.88 mA/cm^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_{OC} of 0.935 V, a J_{SC} of 19.87 mA/cm^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_{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.

Figure 6. J-V curves of perovskite solar cells based on the FTO/c-TiO₂/m-TiO₂/perovskite/spiro-OMeTAD/Ag.

Table 1. Photovoltaic performances summary of the perovskite devices.

Ag Concentration	Voc (V)	Jsc (mA/cm 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 MAPbI₃ 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>, 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 MAPbI₃ 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, Huiying 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.

References

- Jeong, M.; Choi, I.W.; Go, E.M.; Cho, Y.; Kim, M.; Lee, B.; Jeong, S.; Jo, Y.; Choi, H.W.; Lee, J.; et al. Stable perovskite solar cells with efficiency exceeding 24.8% and 0.3-V voltage loss. *Science* **2020**, *369*, 1615–1620. [\[CrossRef\]](#) [\[PubMed\]](#)
- Wang, Y.; Zhang, Y.; Zhang, P.; Zhang, W. High intrinsic carrier mobility and photon absorption in the perovskite CH₃NH₃PbI₃. *Phys. Chem. Chem. Phys.* **2015**, *17*, 11516–11520. [\[CrossRef\]](#)
- Kim, S.H.; Saeed, M.A.; Lee, S.Y.; Shim, J.W. Investigating the Indoor Performance of Planar Heterojunction Based Organic Photovoltaics. *IEEE J. Photovoltaics* **2021**, *11*, 997–1003. [\[CrossRef\]](#)
- Li, M.; Gao, D.; Zhang, B.; Xu, S.; Zhuang, X.; Wang, C.; Yang, L.; Ma, X.; Zheng, S.; Song, H.; et al. Multifunctional Reductive Molecular Modulator toward Efficient and Stable Perovskite Solar Cells. *Sol. RRL* **2021**, *5*, 2100320. [\[CrossRef\]](#)
- Dar, M.I.; Jacopin, G.; Meloni, S.; Mattoni, A.; Arora, N.; Boziki, A.; Zakeeruddin, S.M.; Rothlisberger, U.; Grätzel, M. Origin of unusual bandgap shift and dual emission in organic-inorganic lead halide perovskites. *Sci. Adv.* **2016**, *2*, e1601156. [\[CrossRef\]](#) [\[PubMed\]](#)
- Bi, C.; Zheng, X.; Chen, B.; Wei, H.; Huang, J. Spontaneous Passivation of Hybrid Perovskite by Sodium Ions from Glass Substrates: Mysterious Enhancement of Device Efficiency Revealed. *ACS Energy Lett.* **2017**, *2*, 1400–1406. [\[CrossRef\]](#)
- Li, Y.; Sun, W.; Yan, W.; Ye, S.; Rao, H.; Peng, H.; Zhao, Z.; Bian, Z.; Liu, Z.; Zhou, H.; et al. 50% Sn-Based Planar Perovskite Solar Cell with Power Conversion Efficiency up to 13.6%. *Adv. Energy Mater.* **2016**, *6*, 1601353. [\[CrossRef\]](#)
- Navas, J.; Sánchez-Coronilla, A.; Gallardo, J.J.; Hernández, N.C.; Pinero, J.C.; Alcántara, R.; Fernández-Lorenzo, C.; De los Santos, D.M.; Aguilar, T.; Martín-Calleja, J. New insights into organic-inorganic hybrid perovskite CH₃NH₃PbI₃ nanoparticles. An experimental and theoretical study of doping in Pb²⁺ sites with Sn²⁺, Sr²⁺, Cd²⁺ and Ca²⁺. *Nanoscale* **2015**, *7*, 6216–6229. [\[CrossRef\]](#) [\[PubMed\]](#)
- Zhang, H.; Shang, M.-H.; Zheng, X.; Zeng, Z.; Chen, R.; Zhang, Y.; Zhu, Y. Ba²⁺ Doped CH₃NH₃PbI₃ to Tune the Energy State and Improve the Performance of Perovskite Solar Cells. *Electrochimica Acta* **2017**, *254*, 165–171. [\[CrossRef\]](#)
- Jahandar, M.; Heo, J.H.; Song, C.E.; Kong, K.; Shin, W.S.; Lee, J.C.; Im, S.H.; Moon, S.J. Highly efficient metal halide substituted CH₃NH₃I(PbI₂)₁–X(CuBr₂)X planar perovskite solar cells. *Nano Energy* **2016**, *27*, 330–339. [\[CrossRef\]](#)
- Zhao, W.; Yao, Z.; Yu, F.; Yang, D.; Liu, S. Alkali Metal Doping for Improved CH₃NH₃PbI₃ Perovskite Solar Cells. *Adv. Sci.* **2017**, *5*, 1700131. [\[CrossRef\]](#)
- Nayak, P.K.; Sendner, M.; Wenger, B.; Wang, Z.; Sharma, K.; Ramadan, A.J.; Lovrinčić, R.; Pucci, A.; Madhu, P.K.; Snaith, H.J. Impact of Bi³⁺ Heterovalent Doping in Organic-Inorganic Metal Halide Perovskite Crystals. *J. Am. Chem. Soc.* **2018**, *140*, 574–577. [\[CrossRef\]](#)
- Abdelhady, A.L.; Saidaminov, M.I.; Murali, B.; Adinolfi, V.; Voznyy, O.; Katsiev, K.; Alarousu, E.; Comin, R.; Dursun, I.; Sinatra, L.; et al. Heterovalent Dopant Incorporation for Bandgap and Type Engineering of Perovskite Crystals. *J. Phys. Chem. Lett.* **2016**, *7*, 295–301. [\[CrossRef\]](#)
- Shahbazi, S.; Tsai, C.-M.; Narra, S.; Wang, C.-Y.; Shiu, H.-S.; Afshar, S.; Taghavinia, N.; Diau, E.W.-G. Ag Doping of Organometal Lead Halide Perovskites: Morphology Modification and p-Type Character. *J. Phys. Chem. C* **2017**, *121*, 3673–3679. [\[CrossRef\]](#)
- Abdi-Jalebi, M.; Pazoki, M.; Philippe, B.; Dar, M.I.; Alsari, M.; Sadhanala, A.; Divitini, G.; Imani, R.; Lilliu, S.; Kullgren, J.; et al. Dedoping of Lead Halide Perovskites Incorporating Monovalent Cations. *ACS Nano* **2018**, *12*, 7301–7311. [\[CrossRef\]](#) [\[PubMed\]](#)

16. Si, F.J.; Tang, F.L.; Xue, H.T.; Liu, J.B. Electronic and optical properties of $\text{CH}_3\text{NH}_3\text{PbPb}_{1-x}\text{Ag}_x\text{I}_3$ from the first-principles calculations. *J. Renew. Sustain. Energy* **2018**, *10*, 033504. [[CrossRef](#)]
17. Jeon, N.J.; Noh, J.H.; Yang, W.S.; Kim, Y.C.; Ryu, S.; Seo, J.; Seok, S.I. Compositional engineering of perovskite materials for high-performance solar cells. *Nature* **2015**, *517*, 476–480. [[CrossRef](#)] [[PubMed](#)]
18. Saliba, M.; Matsui, T.; Domanski, K.; Seo, J.-Y.; Ummadisingu, A.; Zakeeruddin, S.M.; Correa-Baena, J.-P.; Tress, W.R.; Abate, A.; Hagfeldt, A.; et al. Incorporation of rubidium cations into perovskite solar cells improves photovoltaic performance. *Science* **2016**, *354*, 206–209. [[CrossRef](#)] [[PubMed](#)]
19. Yang, W.S.; Park, B.-W.; Jung, E.H.; Jeon, N.J.; Kim, Y.C.; Lee, D.U.; Shin, S.S.; Seo, J.; Kim, E.K.; Noh, J.H.; et al. Iodide management in formamidinium-lead-halide-based perovskite layers for efficient solar cells. *Science* **2017**, *356*, 1376–1379. [[CrossRef](#)]
20. Jiang, Q.; Zhao, Y.; Zhang, X.W.; Yang, X.L.; Chen, Y.; Chu, Z.; Ye, Q.F.; Li, X.X.; Yin, Z.G.; You, J.B. Surface passivation of perovskite film for efficient solar cells. *Nat. Photonics* **2019**, *1*, 460–466. [[CrossRef](#)]
21. Guo, Q.; Li, C.; Qiao, W.; Ma, S.; Wang, F.; Zhang, B.; Hu, L.; Dai, S.; Tan, Z. The growth of a $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film using simplified close space sublimation for efficient and large dimensional perovskite solar cells. *Energy Environ. Sci.* **2016**, *9*, 1486–1494. [[CrossRef](#)]
22. Gao, H.; Bao, C.; Li, F.; Yu, T.; Yang, J.; Zhu, W.; Zhou, X.; Fu, G.; Zou, Z. Nucleation and Crystal Growth of Organic–Inorganic Lead Halide Perovskites under Different Relative Humidity. *ACS Appl. Mater. Interfaces* **2015**, *7*, 9110–9117. [[CrossRef](#)]
23. Singh, T.; Miyasaka, T. Stabilizing the Efficiency Beyond 20% with a Mixed Cation Perovskite Solar Cell Fabricated in Ambient Air under Controlled Humidity. *Adv. Energy Mater.* **2017**, *8*, 1700677. [[CrossRef](#)]
24. Yang, F.; Kapil, G.; Zhang, P.; Hu, Z.; Kamarudin, M.A.; Ma, T.; Hayase, S. Dependence of Acetate-Based Antisolvents for High Humidity Fabrication of $\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite Devices in Ambient Atmosphere. *ACS Appl. Mater. Interfaces* **2018**, *10*, 16482–16489. [[CrossRef](#)] [[PubMed](#)]
25. Hao, J.; Hao, H.; Li, J.; Shi, L.; Zhong, T.; Zhang, C.; Dong, J.; Xing, J.; Liu, H.; Zhang, Z. Light Trapping Effect in Perovskite Solar Cells by the Addition of Ag Nanoparticles, Using Textured Substrates. *Nanomaterials* **2018**, *8*, 815. [[CrossRef](#)]
26. You, J.; Yang, Y.; Hong, Z.; Song, T.-B.; Meng, L.; Liu, Y.; Jiang, C.; Zhou, H.; Chang, W.-H.; Li, G. Moisture assisted perovskite film growth for high performance solar cells. *Appl. Phys. Lett.* **2014**, *105*, 183902. [[CrossRef](#)]
27. Wang, F.; Ye, Z.; Sarvari, H.; Park, S.M.; Abtahi, A.; Graham, K.; Zhao, Y.; Wang, Y.; Chen, Z.D.; Li, S. Humidity-insensitive fabrication of efficient perovskite solar cells in ambient air. *J. Power Sources* **2018**, *412*, 359–365. [[CrossRef](#)]
28. Pascoe, A.R.; Meyer, S.; Huang, W.; Li, W.; Benesperi, I.; Duffy, N.W.; Spiccia, L.; Bach, U.; Cheng, Y.-B. Enhancing the Optoelectronic Performance of Perovskite Solar Cells via a Textured $\text{CH}_3\text{NH}_3\text{PbI}_3$ Morphology. *Adv. Funct. Mater.* **2016**, *26*, 1278–1285. [[CrossRef](#)]
29. Lo, M.-F.; Guan, Z.-Q.; Ng, T.-W.; Chan, C.-Y.; Lee, C.-S. Electronic Structures and Photoconversion Mechanism in Perovskite/Fullerene Heterojunctions. *Adv. Funct. Mater.* **2014**, *25*, 1213–1218. [[CrossRef](#)]
30. Luo, D.; Yang, W.; Wang, Z.; Sadhanala, A.; Hu, Q.; Su, R.; Shivanna, R.; Trindade, G.F.; Watts, J.F.; Xu, Z.; et al. Enhanced photovoltage for inverted planar heterojunction perovskite solar cells. *Science* **2018**, *360*, 1442–1446. [[CrossRef](#)] [[PubMed](#)]
31. Poglitsch, A.; Weber, D. Dynamic disorder in methylammoniumtrihalogenoplumbates (II) observed by millimeter-wave spectroscopy. *J. Chem. Phys.* **1987**, *87*, 6373–6378. [[CrossRef](#)]
32. Yang, D.; Yang, R.; Ren, X.; Zhu, X.; Yang, Z.; Li, C.; Liu, S. Hysteresis-Suppressed High-Efficiency Flexible Perovskite Solar Cells Using Solid-State Ionic-Liquids for Effective Electron Transport. *Adv. Mater.* **2016**, *28*, 5206–5213. [[CrossRef](#)] [[PubMed](#)]
33. Bube, R.H. Trap density determination by space-charge-limited currents. *J. Appl. Phys.* **1962**, *33*, 1733–1737. [[CrossRef](#)]
34. Dong, Q.; Fang, Y.; Shao, Y.; Mulligan, P.; Qiu, J.; Cao, L.; Huang, J. Electron-hole diffusion lengths $>175\ \mu\text{m}$ in solution-grown $\text{CH}_3\text{NH}_3\text{PbI}_3$ single crystals. *Science* **2015**, *347*, 967–970. [[CrossRef](#)] [[PubMed](#)]