

DOI: 10.32604/jrm.2022.020535

ARTICLE



Effectively Inhibit Phase Separation to Improve Efficiency and Stability of All-Inorganic Planar CsPbIBr₂ Perovskite Solar Cells

Miao He*, Miao Wu[#], Duofa Wang and Tianjin Zhang*

Ministry of Education Key Laboratory for the Green Preparation and Application of Functional Materials, Collaborative Innovation Center for Advanced Organic Chemical Materials Co-Constructed by the Province and Ministry, Hubei Key Laboratory of Polymer Materials, School of Materials Science and Engineering, Hubei University, Wuhan, 430062, China

*Corresponding Authors: Tianjin Zhang. Email: zhangtj@hubu.edu.cn; Miao He. Email: 20110029@hubu.edu.cn

[#]This author contributed equally to this work and should be considered co-first author

Received: 30 November 2021 Accepted: 25 January 2022

ABSTRACT

The advancement in a power conversion efficiency (PCE) to reach 25%, the inorganic perovskites are being explored intensively as promising optoelectronic materials due to their excellent photovoltaic performance, i.e., thermal stability and efficiency. Lately, the inorganic cesium lead halide perovskite is studied to show enhanced light absorption, however, it suffers from the phase separate into I-rich and Br-rich phase which leads to poor film quality due to difference of electronegativity. Herein, we propose a unique solution of controlling the rate of solvent volatilization followed by gel method to inhibit phase separation effectively to obtain the homogenous and pinhole-free CsPbIBr₂ films with high crystalline quality. In this study, an inverted planar device based on a light absorber of CsPbIBr₂ is prepared to achieve a power conversion efficiency of 8.8% (maintain a stabilized value of 8% in ambient air conditions). Surprisingly, the optimized cell without encapsulation shows excellent long-term stability, as it maintained 90% initial efficiency over 500 h and controlled storage at around 45% relative humidity and 25°C.

KEYWORDS

Inorganic cesium lead halide perovskite; phase separate; high crystalline quality; long-term stability

Nomenclature

J _{sc}	short-circuit current density
Voc	open-circuit voltage

1 Introduction

The ABX₃ type organic-inorganic hybrid perovskites have made amazing breakthroughs in the fields of photovoltaic and optoelectronics. A = organic cations, such as $CH_3NH_3^+$ (MA⁺) and $NH_2CH=NH_2^+$ (FA⁺), B = Pb, Ge, Sn, X = Cl, Br, I. The power conversion efficiency (PCE) of perovskite solar cells (PSCs) has promoted continuously from an initially lower value of 3.8% to a present optimized percentage 25.5% [1–3]. However, due to the presence of humidity which causes the evaporation of the organic parts, the ABX₃ type organic-inorganic hybrid perovskite materials suffer from poor thermal stability [4,5].



This work is licensed under a Creative Commons Attribution 4.0 International License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

As an alternative light absorber for organic-inorganic hybrid perovskites, the inorganic cesium lead halide perovskites have recently attracted tremendous attention due to their excellent thermal stability for photovoltaic (PV) application. Among all the inorganic perovskite solar cells, CsPbBr₃ [6–8] are inspected for good stability and conversion efficiency, however, the light absorption rage for CsPbBr₃ is too narrow, i.e., up to 540 nm of light, which limits the efficiency of the cells. The introduction of halogens into simple CsPbBr₃, i.e., CsPbI₂Br endorse it excellent stability [9–14] than simple CsPbI₃ [15–17]. The CsPbIBr₂ perovskite solar cells perfectly balance the stability and bandgap [18–24] and appear to be the promising candidate among all the previously reported inorganic halide perovskites. However, they become unstable in humidity and the fabricated thin films starts degenerating to yellow phase upon exposure to air. Moreover, the current cell efficiency based on CsPbIBr₂ is generally not high. This dilemma is ascribing primarily to second facts. Firstly, the CsPbIBr₂ films deposited by either conventional one-step or two-step solution routes forms the fine grains with numerous grain boundaries and compositional defects [21,22]. Secondly, the perovskites modified by halides compositions tend to be phase-segregated into iodide and bromide-rich phases [23,24].

In this work, we introduced a solvent-controlled gel method to obtain uniform CsPbIBr₂ thin films containing high bromide by a one-step solution processing method, inspired by literature [21,22]. Moreover, a comprehensive study of the effect of solvent evaporation in-gel method on CsPbIBr₂ crystallization has been conducted which results in the formation homogenous and pinhole-free CsPbIBr₂ films. The planar CsPbIBr₂ solar cells (glass/FTO/SnO₂/CsPbIBr₂/Spiro-OMeTAD/Au) exhibits enhanced charge transport and diffusion, which ultimately optimize the film quality and effectively inhibit phase separation due to the evaporation of the solvent from the film. The CsPbIBr₂ cell exhibits the highest photoelectric conversion efficiency (PCE) of 8.74% placed after 30 min, with the open circuit voltage (V_{oc}) of 1.17 V, the short-circuit current density (J_{sc}) of 10.9 mA·cm⁻² and the fill factor (FF) of 69%, while the PCE of the cell with 0 min of gel treatment is 2.90%, with V_{oc} of 0.90 V, J_{sc} of 7.16 mA·cm⁻² and FF of 45%. Efficiencies of the planar CsPbIBr₂ solar cells (glass/FTO/SnO₂/CsPbIBr₂/Spiro-OMeTAD/Au) reach up to 8.8%.

2 Experimental Methods

2.1 Materials

All chemicals were purchased from commercial sources. The tin dioxide (SnO₂) colloidal precursors purchased from Alfa Aesar. The chemical purity of cesium iodide (CsI) and lead bromide (PbBr₂) reach 99.999% reaches, the above two were purchased from Aladdin Chemicals Reagent Co., Ltd., China. Dimethyl sulfoxide (DMSO, Sigma-Aldrich). The FTO glass and Spiro-OMeTAD were purchased from Advanced Election Technology Co., Ltd., China. Conductive carbon paste was obtained from Shanghai MaterWin New Materials Co., Ltd., China.

2.2 Device Fabrication

Deionized water, acetone, and alcohol were used progressively to wash the substrate FTO glass before spin coating. Then, FTO substrate was deposited by SnO_2 layer using spin coating at 4000 rpm for 30 s and annealed at 150°C for 30 min. The 1 M solution of CsPbIBr₂ perovskite precursor was prepared, with a pure solution of DMSO. Afterwards, the CsPbIBr₂ perovskite film was deposited by a single-step method spin coating 2000 rpm in glove box for 60 s. After deposition of CsPbIBr₂ layer, it was placed in glove box and allowed the formation of gel for different times. The films were then annealed at 280°C for 10 min. After that, hole transporting layer was obtained by spin coating the 1 ml of Spiro-OMeTAD/chlorobenzene solution on perovskite/SnO₂/FTO/glass at 4000 rpm for 30 s, Spiro-OMeTAD/chlorobenzene solution contains 72.3 mg Spiro-OMeTAD and 17.5 μ l lithium bis (trifluoromethanesulphonyl) imide/acetonitrile (260 mg/ml) and 28.8 μ l 4-tert-butylpyridine. Eventually, the 100 nm of the gold electrode was obtained by thermal evaporation using a shadow mask.

2.3 Characterization

The prepared device was characterized by X-ray diffractometer (D8 advance, Bruker, Karlsruhe, Germany) with radiation of Cu (K α) at 40 kV and 40 mA ($\lambda = 1.54178$ Å) for the structural and crystallographic analysis. The absorption spectrum was detected by the Ultraviolet-3600 spectrophotometer (Shimadzu, Kyoto, Japan) with working range of 400–800 nanometers. A transient spectroscopy system (FluoTime 300, PICOQUANT GMBH, Germany) was used to obtained the photoluminescence (PL) and PL lifetimes with a 485 nm laser excitation source. The morphological analysis of the sample was explored by a field emission scanning electron microscope (SEM, JSM-6700F, Japan Electronics Corporation, Tokyo, Honshu, Japan). Photocurrent density-voltage (J-V) curves were acquired using a Keithley 2400 (Keithley Instruments, Inc., Cleveland, OH, USA) source meter under 1.5 G AM optical filter one-sun illumination provided by a solar simulator 91192–1000 (Newport Corporation-Oriel Instruments, Mountain View, CA, USA) on the active area of 0.1 cm² of the cell.

3 Results and Discussion

Typically, the maximum solubility of bromide ion in N, N-dimethylformamide (DMF) precursor solutions is approximately up to 0.40–43 M [13]. Therefore, we selected the stronger polarity dimethyl sulfoxide (DMSO) as the only solvent to increase the solubility of the bromides and thus increase the precursor concentration. For the solvents with high boiling point, i.e., DMSO (189°C), it is hard to escape from the precursor film after spin-coating. It has been demonstrated that the residual DMSO could enhance the mass transport and diffusion in the annealing process which significantly promote perovskite grain growth [15,21]. Therefore, the aims of this research are focused on studying the crystal formation behavior of CsPbIBr₂ perovskites by researching the crystal structure, surface morphology, and chemical state of CsPbIBr₂ films and then prepare highly efficient CsPbIBr₂ planar heterojunction solar cells. This research emphasizes the key role of the evaporation rate of the solvent for the preparation of the pure phase of CsPbIBr₂ perovskites, which greatly improves the performance and phase stability of CsPbIBr₂ planar heterojunction solar cells.

The schematic illustration of CsPbIBr₂ perovskite thin film preparation is demonstrated in Fig. 1a. The time-dependent gelation of perovskite thin films reveals that less dark thin films exhibits excellent transmission. The photograph of CsPbIBr₂ perovskite thin films with different gelation times from 0 to 50 min could be seen in Fig. S1. Fig. 1b shows the X-ray diffraction (XRD) patterns of annealed perovskite thin films placed after 0 and 30 min. It is found that the (100) and (200) crystal planes of annealed perovskite thin films appeared at 14.6° and 29.5° both before and after placement, but there are small peaks that appear around the main peak when perovskite thin films are directly annealed. Moreover, we performed a quantitative analysis of these peaks, and the corresponding XRD is shown in Fig. S2, which further proves that phase separation can be effectively suppressed by the way of placement. Fig. 1c shows the PL spectrum of the two annealed perovskite thin films which deposited on SnO_2 layer. SnO_2 is electron transport layer. The PL intensity of the perovskite film with gel 30 min is much lower than perovskite film with gel 0 min, which indicates that carrier transport performance is more efficient in the perovskite film with gel 30 min. Similarly, in addition to the photoluminescence peak around 600 nm, it also has a small photoluminescence peak near 700 nm when the perovskite thin film is directly annealed. This result indicates that the carrier transport performance of the perovskite film with gel 0 min is inferior to that with gel 30 min according to the PL peak values. These results further affirm the XRD results. Figs. 1d and 1e exhibit the scanning electron microscope (SEM) images of the surface morphology of the two annealed perovskite thin films. The grains are abnormally large when the perovskite thin films are directly annealed. This phenomenon is similar to that when chemically synthesizing single crystals. Direct annealed liquid films have more solvents and large spaces, which lead to abnormally large grains. Also, due to the poor ductility of DMSO, the film is not completely covered [13, 14]. When the perovskite film

is annealed after being placed for 30 min, its surface morphology becomes significantly denser and flatter, which indicates that it is also beneficial to the growth of the film while suppressing phase separation by placing it.



Figure 1: (a) Schematic illustration of perovskite thin film preparation. (b) XRD patterns of annealed perovskite thin films for 0 and 30 min gelation. (c) Steady state PL spectra of annealed perovskite thin films. SEM images of annealed perovskite thin films placed for (d) 0 min and (e) 30 min

In order to explain the changes in perovskite film morphology, we further studied the intermediate process of film growth. Fig. 2a shows the XRD pattern of the gelation film without annealing placed at different times. It can be seen that when the placing time is 0 min, there are no characteristic peaks of PbX₂(DMSO) (X is I and Br) adducts in intermediates DMSO-PbX₂-CsI in the XRD test. With the extension of the place time, the characteristic peaks can be seen at 10.2° and 12.9° [13]. When the placing time is extended to 50 min, the peaks of adducts disappear. Fig. 2b shows the UV-visible absorption spectra of the gelation film gradually increases with the extension of the placing time. And the film can hardly absorb light when it places for 0 min, which is consistent with the corresponding XRD

pattern. Moreover, the photographs of the samples are shown in Fig. S1. It can be seen that the color of the film gradually becomes darker as the placing time increases, and the color of the film is transparent when left for 0 min, further explaining why the absorption value is almost zero. These phenomena all indicate that the perovskite film has self-assembly characteristics during the placement process due to the fluidity of the solution and the electronegativity between molecules [25].



Figure 2: (a) X-ray diffraction (XRD) pattern of gelation films placed for different times before annealing. The diffraction peaks labeled as "#" are $PbX_2(DMSO)$ at 10.2° and 12.9°. The gelation films changes from 0 to 50 min before annealing. (b) UV-visible absorption spectra of perovskite films with gelation time ranging

To further reveal the self-assembly process of films during placement, we inspect the SEM images of the liquid films placed at different time as shown in Fig. 3. These images clearly reveal the differences in the growth process of the gelation films. The Fig. 3a reveals the morphology of the film placed at 0 min which mostly contains the woven materials. Combined with the results of the XRD test, we analyzed that this woven material was a liquid material without the formation of any perovskite crystals. When the film is placed for 10 min as shown in Fig. 3b, in addition to the gradual reduction of the woven materials and their gradual broadening, a large amount of bulk material appeared. Combined with the corresponding XRD diffraction peaks, we speculate that the bulk material formed is perovskite at this time. Because of the absence of annealing, there are adducts in intermediates DMSO-PbX₂-CsI in the film growth process. Such abnormally large grains are also caused by the secondary crystallization of the film during the growth process due to the presence of the intermediates. The gelation film becomes dense and uniform when it is placed for 30 min as illustrated in Fig. 3c, and it still has a small amount of intermediates at this time (peaks of PbX₂ (DMSO) still present in XRD), which provides a flat and dense surface for the growth of the film during annealing, this is consistent with the results of the SEM measurements in Fig. 1. Fig. 3d shows the morphology of the gelation film places for 50 min, which is different from the morphology of the gelation film places for 30 min. The yellow circle in the illustration shows that the gelation film surface is not smooth before annealing, which is harmful to the formation of dense and flat perovskite film after annealing. Also, the steady photoluminescence spectra (Fig. S3) indicates that the carrier transport performance of 50 min is inferior to those of 30 min according to the experimental results of intensity of the absorption peak, we analyze that the steady photoluminescence (PL) spectra intensities of perovskite films with transport layer exhibit a twofold increase when increasing the gelation time from 30 to 50 min. Such enhanced PL intensity demonstrates an increase in the rate of nonradiative charge carrier recombination, possibly due to an addition in the grain boundaries, which serve as sites of nonradiative recombination [26]. This finding is consistent with the results of the SEM measurements in Figs. 3c and 3d indirectly.



Figure 3: SEM images of the gelation films without annealing and placing for (a) 0 min (b) 10 min (c) 30 min (d) 50 min

As is well-known, PbX_2 is a kind of Lewis acid, while CsI and DMSO are Lewis bases because of the presence of lone pair-electron donors (iodide for CsI and oxygen for DMSO), which tend to interact with PbX_2 to form adducts [27–30]. From the above descriptions, the precursor film of gel at different times can be classified into four distinct morphologies: precursor film without any apparent gel, partly gel film, fully uniform transparent gelation film and gelation film with perovskite. Film gelation by the residual DMSO significantly enhance the mass transport and diffusion, which ultimately improve the film quality and effectively inhibit phase separation due to the evaporation of the solvent from the film, as described in Fig. 4.

After annealing without any apparent gel or partly gel, as the DMSO volatilizing, several pin holes or a less pin hole film can be formed with obvious I-rich and Br-rich phase or phase separation weakened, as described in earlier section. When annealed after gel sufficient time, due to the weak Van der Waal-type interaction, DMSO molecules will be inserted between the adjacent planes of PbX₂, resulting in an increase in the interlayer distance of PbX₂, which forms DMSO-coordination PbX₂, along the C-axis [24]. This facilitates the insertion of CsI and good coordination with PbX₂. Then the formation of a large amount of intermediates PbX₂-DMSO-CsI occurs through the spin coating process, similar to that in MAPbI₃ [25]. However, when the gelation time is too long (50 min), because the gelation film reaches dissolution limit, which led to an uneven surface of the gelation film, and more defects form inside the annealed perovskite film, this can be explained by Figs. 3 and S3, which has mentioned above.



Figure 4: The schematic diagram of the crystal growth kinetics of CsPbIBr₂ films

Fig. 5a is the reverse scanned J-V curves of the annealed CsPbIBr₂ PSCs placed after 0 and 30 min. The CsPbIBr₂ cell exhibits the highest PCE of 8.74% placed after 30 min, with the open circuit voltage (V_{oc}) of 1.17 V, the short-circuit current density (J_{sc}) of 10.90 mA·cm⁻² and the fill factor (FF) of 69%, as described in Tables 1 and 2 shows the performance of the CsPbIBr₂ PSC placed after 0 min. While the PCE of the device without placement is 2.90%, V_{oc} is 0.90 V, J_{sc} is 7.16 mA·cm⁻² and FF is 45%. In Fig. 5b, we show histograms of the J-V scan PCE of 43 solar cells annealing after placed 30 min. The other PV parameters including J_{sc} , V_{oc} , and PCE at different placement times are shown in Fig. S4, from which can be seen that the V_{oc} , J_{sc} , and PCE are all enhanced after being placed 30 min. In Fig. 5c, long-term stability is investigated by placing the non-encapsulated device in the air at room temperature. We can see that the PSC annealed after being left for 30 min can maintain 90% of the initial PCE after 30 h of aging, as described in Fig. S5, X-ray diffraction (XRD) pattern of the optimized perovskite films after aging for 500 h in discates that phase separation was suppressed. When the cell is continuously irradiated under AM1.5 sunlight, the control device loses 46% of the PCE, while it maintains 97% of the initial value for the PSC after 30 min of gel treatment (Fig. 5d).



Figure 5: (a) Reverse scanned J-V curves of the CsPbIBr₂ PSCs after 0 and 30 min of gel treatment. (b) Histogram of current density-voltage (J-V) scan efficiencies of 43 solar cells after 30 min of gel treatment. (c) Normalized PCE of the devices aged for 500 h in an air environment after 0 and 30 min of gel treatment. (d) Stability characterization of the devices after 30 min of gel treatment

Table 1: The performance parameters of device after 30 min of gel treatment

Device	PCE(%)	P _{max} (mW)	$V_{oc}(V)$	$J_{sc}(mA \cdot cm^{-2})$	FF(%)
glass/FTO/SnO ₂ /CsPbIBr ₂ /Spiro-OMeTAD/Au	8.74	8.80	1.17	10.90	69

Device	PCE(%)	P _{max} (mW)	V _{oc} (V)	$J_{sc}(mA \cdot cm^{-2})$	FF(%)
glass/FTO/SnO ₂ /CsPbIBr ₂ /Spiro-OMeTAD/Au	2.90	2.89	0.90	7.16	45

Table 2: The performance parameters of device after 0 min of gel treatment

4 Conclusions

In summary, homogenous and pinhole-free CsPbIBr₂ thin films with high crystalline quality was successfully fabricated using gelation technique for perovskite solar cells. The uniqueness of this work is controlling the rate of solvent volatilization to inhibit phase separation effectively to obtain the homogenous and defect free crystalline structure. More importantly, an inverted planar device based on a light absorber of CsPbIBr₂ achieves a power conversion efficiency of 8.8%, and maintain a stabilized value of 8% in ambient air conditions. Of note, the optimized cell without encapsulation shows excellent long-term stability, as it maintained 90% initial efficiency over 500 h and controlled storage at around 45% relative humidity and 25°C. This approach will further insights the effectiveness of gelation technique towards the excellent defect free morphology of the films, and the performance of the devices.

Funding Statement: This work was supported by the National Natural Science Foundation of China (Nos. 11174071, 11304088, and 51372180), and Special Technical Innovation Project of Hubei Province (Nos. 2016AAA035 and 20178ACA088).

Conflicts of Interest: The authors declare that they have no conflicts of interest to report regarding the present study.

References

- 1. Kojima, A., Teshima, K., Shirai, Y., Miyasaka, T. (2009). Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. *Journal of the American Chemical Society*, *131(17)*, 6050–6051. DOI 10.1021/ja809598r.
- 2. Yang, W. S., Park, B. W., Jung, E. H., Jeon, N. J., Kim, Y. C. et al. (2017). Iodide management in formamidinium-leadhalide–based perovskite layers for efficient solar cells. *Science*, *356(6345)*, 1376–1379. DOI 10.1126/science.aan2301.
- 3. Yoo, J. J., Seo, G., Chua, M. R., Park, T. G., Lu, Y. L. et al. (2021). Efficient perovskite solar cells via improved carrier management. *Nature, 590,* 587–593. DOI 10.1038/s41586-021-03285-w.
- 4. Berhe, T. A., Su, W. N., Chen, C. H., Pan, C. J., Cheng, J. H. et al. (2016). Organometal halide perovskite solar cells: Degradation and stability. *Energy & Environmental Science*, *9*, 323–356. DOI 10.1039/C5EE02733K.
- Conings, B., Drijkoningen, J., Gauquelin, N., Babayigit, A., D'Haen, J. et al. (2015). Intrinsic thermal instability of methylammonium lead trihalide perovskite. *Advanced Energy Materials*, 5(15), 1500477. DOI 10.1002/ aenm.201500477.
- 6. Liang, J., Wang, C. X., Wang, Y. R., Xu, Z. R., Lu, Z. P. et al. (2016). All-inorganic perovskite solar cells. *Journal* of the American Chemical Society, 138(49), 15829–15832. DOI 10.1021/jacs.6b10227.
- 7. Duan, J. L., Zhao, Y. Y., He, B. L., Tang, Q. W. (2018). High-purity inorganic perovskite films for solar cells with 9.72% efficiency. *Angewandte Chemie*, 130(14), 3849–3853. DOI 10.1002/ange.201800019.
- Chang, X. W., Li, W. P., Zhu, L. Q., Liu, H. C., Geng, H. F. et al. (2016). Carbon-based CsPbBr₃ perovskite solar cells: All-ambient processes and high thermal stability. *ACS Applied Materials & Interfaces*, 8(49), 33649–33655. DOI 10.1021/acsami.6b11393.
- 9. Mariotti, S., Hutter, O. S., Phillips, L. J., Yates, P. J., Kundu, B. et al. (2018). Stability and performance of CsPbI₂Br thin films and solar cell devices. *ACS Applied Materials & Interfaces*, *10(4)*, 3750–3760. DOI 10.1021/acsami.7b14039.
- 10. Chen, Y. X., Shi, T. T., Liu, P. Y., Xie, W. G., Chen, K. et al. (2019). The distinctive phase stability and defect physics in CsPbI₂Br perovskite. *Journal of Materials Chemistry A*, *7*(35), 20201–20207. DOI 10.1039/C9TA04839A.
- 11. Lau, C. F. J., Zhang, M., Deng, X. F., Zheng, J. H., Bing, J. M. et al. (2017). Strontium-doped low-temperature-processed CsPbI₂Br perovskite solar cells. *ACS Energy Letters*, *2(10)*, 2319–2325. DOI 10.1021/acsenergylett.7b00751.
- 12. Patil, J. V., Mali, S. S., Hong, C. K. (2020). A-site rubidium cation-incorporated CsPbI₂Br all-inorganic perovskite solar cells exceeding 17% efficiency. *Solar RRL, 4(7),* 2000164. DOI 10.1002/solr.202000164.
- Yin, G. N., Zhao, H., Jiang, H., Yuan, S. H., Niu, T. Q. et al. (2018). Precursor engineering for all-inorganic CsPbI₂Br perovskite solar cells with 14.78% efficiency. *Advanced Functional Materials*, 28(39), 1803269. DOI 10.1002/adfm.201803269.
- Liu, C., Li, W. Z., Zhang, C. L., Ma, Y. P., Fan, J. D. et al. (2018). All-inorganic CsPbI₂Br perovskite solar cells with high efficiency exceeding 13%. *Journal of the American Chemical Society*, 140(11), 3825–3828. DOI 10.1021/jacs.7b13229.
- Wang, P. Y., Zhang, X. W., Zhou, Y. Q., Jiang, Q., Ye, Q. F. et al. (2018). Solvent-controlled growth of inorganic perovskite films in dry environment for efficient and stable solar cells. *Nature Communications*, 9, 2225. DOI 10.1038/s41467-018-04636-4.
- Wang, Q., Zheng, X. P., Deng, Y. H., Zhao, J. J., Chen, Z. L. et al. (2017). Stabilizing the α-phase of CsPbI₃ perovskite by sulfobetaine zwitterions in one-step spin-coating films. *Joule*, 1(2), 371–382. DOI 10.1016/j. joule.2017.07.017.
- 17. Lau, C. F. J., Deng, X. F., Zheng, J. H., Kim, J., Zhang, Z. L. et al. (2018). Enhanced performance via partial lead replacement with calcium for a CsPbI₃ perovskite solar cell exceeding 13% power conversion efficiency. *Journal of Materials Chemistry A*, *6*, 5580–5586. DOI 10.1039/C7TA11154A.

- Lau, C. F. J., Deng, X. F., Ma, Q. S., Zheng, J. H., Yun, J. S. et al. (2016). CsPbIBr₂ perovskite solar cell by sprayassisted deposition. ACS Energy Letters, 1(3), 573–577. DOI 10.1021/acsenergylett.6b00341.
- Ma, Q. S., Huang, S. J., Wen, X. M., Green, M. A., Ho-Baillie, A. W. Y. (2016). Hole transport layer free inorganic CsPbIBr₂ perovskite solar cell by dual source thermal evaporation. *Advanced Energy Materials*, 6(7), 1502202. DOI 10.1002/aenm.201502202.
- Yu, Y. T., Yang, S. H., Chou, L. H., Osaka, I., Wang, X. F. et al. (2021). One-step spray-coated all-inorganic CsPbI₂Br perovskite solar cells. ACS Applied Energy Materials, 4(6), 5466–5474. DOI 10.1021/acsaem.1c00054.
- Zhu, W., Zhang, Q. N., Chen, D. Z., Zhang, Z. Y., Lin, Z. H. et al. (2018). Intermolecular exchange boosts efficiency of air-stable, carbon-based all-inorganic planar CsPbIBr₂ perovskite solar cells to over 9%. *Advanced Energy Materials*, 8(30), 1802080. DOI 10.1002/aenm.201802080.
- Liu, C., Li, W. Z., Chen, J. H., Fan, J. D., Mai, Y. H. et al. (2017). Ultra-thin MoOx, as cathode buffer layer for the improvement of all-inorganic CsPbIBr₂, perovskite solar cells. *Nano Energy*, 41, 75–83. DOI 10.1016/j. nanoen.2017.08.048.
- Li, W., Rothmann, M. U., Liu, A., Wang, Z. Y., Zhang, Y. P. et al. (2017). Phase segregation enhanced ion movement in efficient inorganic CsPbIBr₂ solar cells. *Advanced Energy Materials*, 7(20), 1700946. DOI 10.1002/aenm.201700946.
- Wang, Z., Baranwal, A. K., kamarudin, M. A., Ng, C. H., Pandey, M. et al. (2019). Xanthate-induced sulfur doped all-inorganic perovskite with superior phase stability and enhanced performance. *Nano Energy*, 59, 258–267. DOI 10.1016/j.nanoen.2019.02.049.
- Bai, Y., Xiao, S., Hu, C., Zhang, T., Meng, X. Y. et al. (2017). A pure and stable intermediate phase is key to growing aligned and vertically monolithic perovskite crystals for efficient PIN planar perovskite solar cells with high processibility and stability. *Nano Energy*, 34, 58–68. DOI 10.1016/j.nanoen.2017.02.019.
- 26. Quilettes, D. W. D., Vorpahl, S., Stranks, S. D., Nagaoka, H., Eperon, G. E. et al. (2015). Impact of microstructure on local carrier lifetime in perovskite solar cells. *Science*, *348(6235)*, 683–686. DOI 10.1126/science.aaa5333.
- Xu, C. Z., Zhang, Z., Zhang, S. C., Si, H. N., Ma, S. F. et al. (2021). Manipulation of perovskite crystallization kinetics via lewis base additives. *Advanced Functional Materials*, 31(13), 2009425. DOI 10.1002/ adfm.202009425.
- Ye, L. F., Wang, H. Y., Wei, Y., Guo, P. F., Yang, X. K. et al. (2019). Acetate-based crystallization kinetics modulation of CsPbI₂Br for improved photovoltaic performance. ACS Applied Energy Materials, 3(1), 658– 665. DOI 10.1021/acsaem.9b01859.
- Chen, H., Liu, T., Zhou, P., Li, S., Ren, J. et al. (2019). Efficient bifacial passivation with crosslinked thioctic acid for high-performance methylammonium lead iodide perovskite solar cells. *Advanced Materials*, 32(6), 1905661. DOI 10.1002/adma.201905661.
- Zhao, H., Yang, S. M., Han, Y., Yuan, S. H., Jiang, H. et al. (2019). A high mobility conjugated polymer enables air and thermally stable CsPbI₂Br perovskite solar cells with an efficiency exceeding 15%. *Advanced Materials Technologies*, 4(9), 1900311. DOI 10.1002/admt.201900311.

Supplementary Figures



Figure S1: The photograph of CsPbIBr₂ perovskite thin films with different gelation times from 0 to 50 min



Figure S2: X-ray diffraction (XRD) pattern of perovskite films with different gel times



Figure S3: Steady photoluminescence (PL) spectra of perovskite films with transport layer during different gelation times from 0 to 50 min



Figure S4: (a) J_{sc} , (b) V_{oc} , and (c) PCE statistical figures of cells without encapsulation at different placement times



Figure S5: X-ray diffraction (XRD) pattern of the optimized perovskite films after aging for 500 h