


ARTICLE

DOI: 10.1038/s41467-018-04636-4

OPEN

Solvent-controlled growth of inorganic perovskite films in dry environment for efficient and stable solar cells

Pengyang Wang^{1,2}, Xingwang Zhang^{1,2}, Yuqin Zhou², Qi Jiang^{1,2}, Qiufeng Ye^{1,2}, Zema Chu¹, Xingxing Li^{1,2}, Xiaolei Yang¹, Zhigang Yin^{1,2} & Jingbi You ^{1,2}

Inorganic halide perovskites such as cesium lead halide are promising due to their excellent thermal stability. Cesium lead iodide (CsPbI₃) has a bandgap of 1.73 eV and is very suitable for making efficient tandem solar cells, either with low-bandgap perovskite or silicon. However, the phase instability of CsPbI₃ is hindering the further optimization of device performance. Here, we show that high quality and stable α -phase CsPbI₃ film is obtained via solvent-controlled growth of the precursor film in a dry environment. A 15.7% power conversion efficiency of CsPbI₃ solar cells is achieved, which is the highest efficiency reported for inorganic perovskite solar cells up to now. And more importantly, the devices can tolerate continuous light soaking for more than 500 h without efficiency drop.

¹Key Laboratory of Semiconductor Materials Science, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China. ²College of Materials Science and Opto-electronic Technology, University of Chinese Academy of Sciences, Beijing 100049, China. Correspondence and requests for materials should be addressed to J.Y. (email: jyou@semi.ac.cn)

Halide perovskite semiconductors used in photovoltaic devices were reported by Miyasaka et al. in 2009. The power conversion efficiency (PCE) has increased rapidly to more than 20% in the past several years^{1–14}. And the large area module of perovskite solar cells was also demonstrated recently¹⁵. Traditional perovskite solar cells were mainly based on organic–inorganic hybrid materials such as methylammonium lead halide (MAPbX₃, X = Cl, Br, I) and formamidinium lead halide (FAPbX₃, X = Cl, Br, I), or their mixture^{1–14}. In addition to humidity instability, the organic–inorganic hybrid perovskite materials also suffer from poor thermal stability due to easy evaporation of the organic parts^{16, 17}.

Inorganic halide perovskite (CsPbX₃) (X = Cl, Br, I) could be more thermally stable, it was found that CsPbX₃ can sustain temperatures exceeding 400 °C without any phase degradation^{18, 19}. This could be the reason of the significant photostability improvement of perovskite solar cells, while incorporating inorganic metal cations such as Cs or Rb into the organic cations in MAPbI₃ or FAPbI₃ perovskites^{11, 20–23}. In addition to the excellent thermal stability, inorganic perovskite such as CsPbI₃ showed an optical bandgap of 1.73 eV^{24, 25}, which is an ideal material to configure tandem cells combined with either silicon or low-bandgap perovskite^{26–30}. Even though similar bandgap could also be obtained from organic/inorganic perovskite by mixture halide strategy, halide segregation could be a critical issue for affecting photostability of the devices, while the

halide dopant is more than 30% (such as FAPbI_{0.6}Br_{0.4})²⁷. Therefore, it is very meaningful to achieve high efficiency and stable CsPbI₃ solar cells. However, it was found that the α -phase (black phase) of CsPbI₃ could be rapidly degraded to non-photoactive δ -phase (yellow phase) in an ambient environment with moisture^{25, 31–35}. It has been explained that the moisture can effectively introduce vacancies in the crystal lattice and lower the free-energy barrier to nucleation, and trigger the phase transition of CsPbI₃ perovskite even at room temperature^{32, 33}.

Previously, there are several efforts to stabilize the α -phase of CsPbI₃ to make efficient solar cells^{25, 34–42}, such as tuning the tolerance factor of perovskite structure by partially substituting iodide with bromide to form CsPbI₂Br or CsPbIBr₂^{34–37}, reducing the crystal size^{25, 40, 42}, or introducing intermediate phase such as Cs₄PbI₆⁴¹. All these efforts push the efficiency of inorganic perovskite solar cells to around 10%. Recently, during the preparation of this manuscript, significant progresses were witnessed, around 13% PCE of CsPbI₃-based solar cells were reported by either doping B site in ABX₃ perovskite structure⁴³ or by passivating/stabilizing CsPbI₃ quantum dot colloid via organic salt molecular^{44, 45}. Even though, there is still a large room for further improving the PCE of CsPbI₃ solar cells. To deliver higher efficiency of CsPbI₃-based perovskite solar cells, two issues must be resolved. One is forming stable α -phase of CsPbI₃ films³⁴. Another one is obtaining the high quality of CsPbI₃ layer, similar to the initial development of organic–inorganic perovskite solar

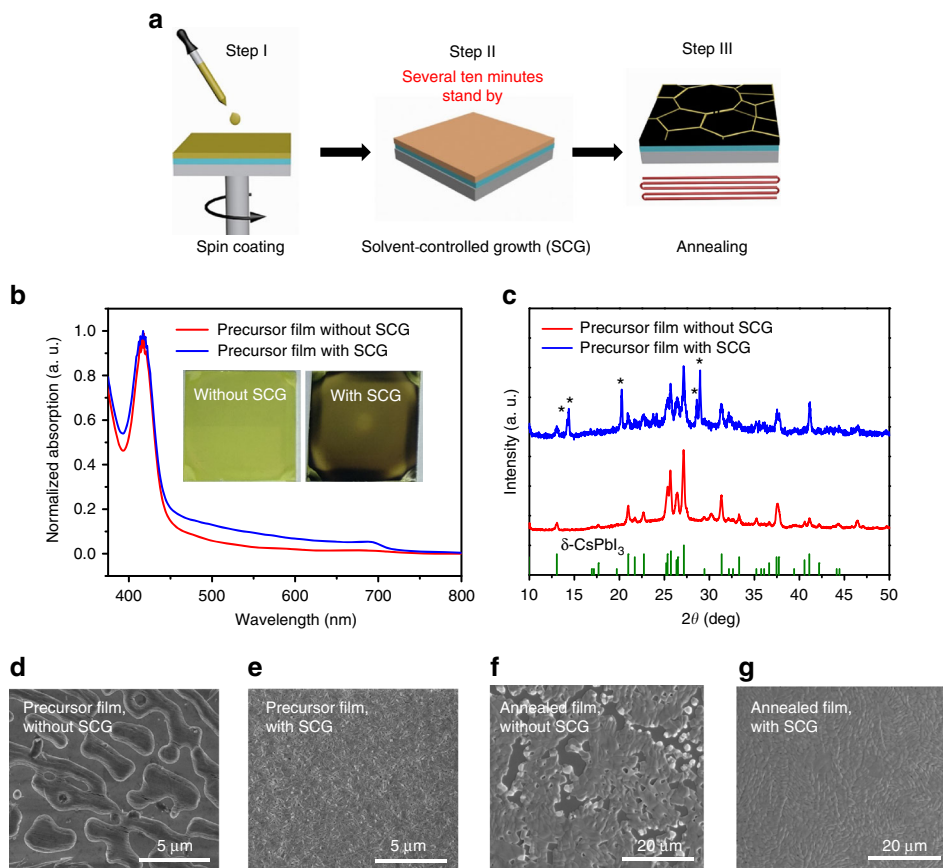


Fig. 1 Solvent-controlled growth (SCG) for CsPbI₃ deposition. **a** Schematic illustration of CsPbI₃-perovskite crystallization procedures via solvent-controlled growth (SCG). **b** Normalized absorption of CsPbI₃-precursor films with and without SCG, inset shows the precursor film images without and with SCG. **c** X-ray diffraction (XRD) pattern of CsPbI₃-precursor films without and with solvent-controlled growth (SCG). Without SCG, the diffraction peaks are mainly from the δ -phase CsPbI₃, while after SCG, part of δ -phase CsPbI₃ was transferred into β -phase CsPbI₃ (a slight distorted α -phase CsPbI₃). The diffraction peaks labeled as "*" are the diffraction peaks from the β -phase CsPbI₃. **d, e** Scanning electron microscopy (SEM) image of CsPbI₃ perovskite precursor film without and with SCG, respectively, scale bar: 5 μ m. **f, g** SEM images of annealed CsPbI₃ perovskite precursor films without and with SCG, respectively, scale bar: 20 μ m

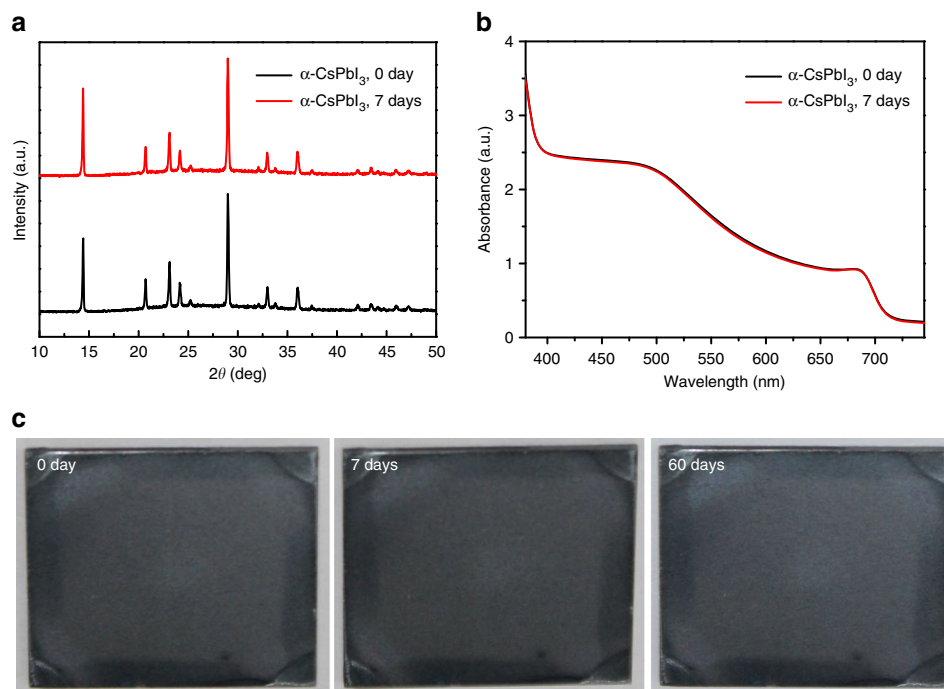


Fig. 2 Phase stability of α -CsPbI₃ films in dry nitrogen environment. **a** X-ray diffraction (XRD) of CsPbI₃-precursor films annealed at 350 °C for 10 min, all the diffraction peaks from the α -phase of CsPbI₃, and also the XRD pattern of α -CsPbI₃ after storing in a dry nitrogen box for 7 days. **b** Absorption of the α -phase of CsPbI₃ films before and after 7 days of storage in dry nitrogen. **c** Images of annealed CsPbI₃ films stored in dry nitrogen box for different days

cells, the pinholes, and grain boundary in the active layer usually leading to serious recombination and also poor device performance^{46–48}.

Herein, we show a simple solvent-controlled growth (SCG) method to produce high-quality α -phase CsPbI₃ perovskite thin films. To avoid phase transformation of CsPbI₃ films, from black to yellow phase triggered by moisture^{25, 31–33}, we processed the films in dry nitrogen environment, and stable α -phase of CsPbI₃ was obtained. Adopting the high quality and stable α -phase of CsPbI₃ as absorption layer to configure the solar cells, we achieved a PCE of 15.7% and a certified PCE of 14.67%, which represent the highest level of inorganic perovskite solar cells so far. More importantly, our preliminary results show that the CsPbI₃ solar cells own excellent photostability, the device can tolerate more than 500 h of continuous light soaking, and no significant efficiency drop is observed.

Results

Growth of CsPbI₃ films. We prepared the CsPbI₃-precursor films by spin-coating a solution containing PbI₂ and CsI in a mixture solvent of N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). It is expected that high boiling point solvent, DMSO (189 °C), could not easily completely escape from the precursor film after spin-coating. The residual DMSO could enhance the mass transport and diffusion, which could improve the film quality if we slow down the evaporation rate of the solvent. Based on this idea, we stand by the precursor films in the nitrogen glove box for several ten minutes before annealing, we named this process as SCG (Fig. 1a).

The spin-coated precursor films without SCG showed greenish-yellow color (inset of Fig. 1b, Supplementary Fig. 1). After SCG, we observed that the color of the precursor films gradually changed from greenish-yellow to light black during SCG (inset of Fig. 1b, Supplementary Fig. 1). As a result, in addition to the absorption edge at 460 nm, an absorption in the

visible region was observed, indicating that an additional phase has been formed during SCG. The absorption edge of this additional phase is located at 720 nm, which is similar to α -phase CsPbI₃ (713 nm) (Figs. 1b and 2b), but with a little red-shift. X-ray diffraction (XRD) results further confirmed the appearance of the additional phase after SCG. For the precursor films without SCG, only the diffraction peaks from the δ -phase CsPbI₃ were observed. While for the precursor films with SCG, except for the diffraction peaks from the δ -phase CsPbI₃, obvious diffraction peaks located at 14.2°, 14.4°, 20.2°, 28.6°, and 29.0° were observed. These diffraction peaks could be from β -phase CsPbI₃, which is also a black phase, while owns a slightly distorted crystal structure compared with α -phase CsPbI₃⁴⁹ (Figs. 1c and 2a, Supplementary Fig. 2b). Similar β -phase CsPbI₃ has been observed while using phenylethylammonium-stabilized CsPbI₃ films⁴⁹. The partial phase change from the δ -phase CsPbI₃ to the β -phase CsPbI₃ after SCG indicated that the precursor materials were diffused and the precursor film was reconstructed during solvent evaporation. This enhanced mass transport process could be in favor of the uniform and high-quality film formation.

Accomplished with the formation of an additional phase in the precursor film, we also found that the precursor film became more continuous, and the pinholes in the precursor films have been filled after SCG (Fig. 1d, e). The improvement of morphology also indicated the enhanced diffusion and also the mass transportation during SCG. This will be helpful for obtaining high-quality α -phase CsPbI₃ perovskite film after annealing. Similar SCG method has been adopted in organic solar cells, while high boiling point solvent such as dichlorobenzene is used, and the enhanced polymer crystallization is observed⁵⁰, while the crystal growth kinetic seems different from the SCG methods shown in this study.

As we expected, the annealed CsPbI₃-perovskite films with SCG are free of pinholes and showed crystal size above 5 μ m (Fig. 1g, Supplementary Fig. 3). However, the CsPbI₃-perovskite films obtained without SCG usually showed a large number of

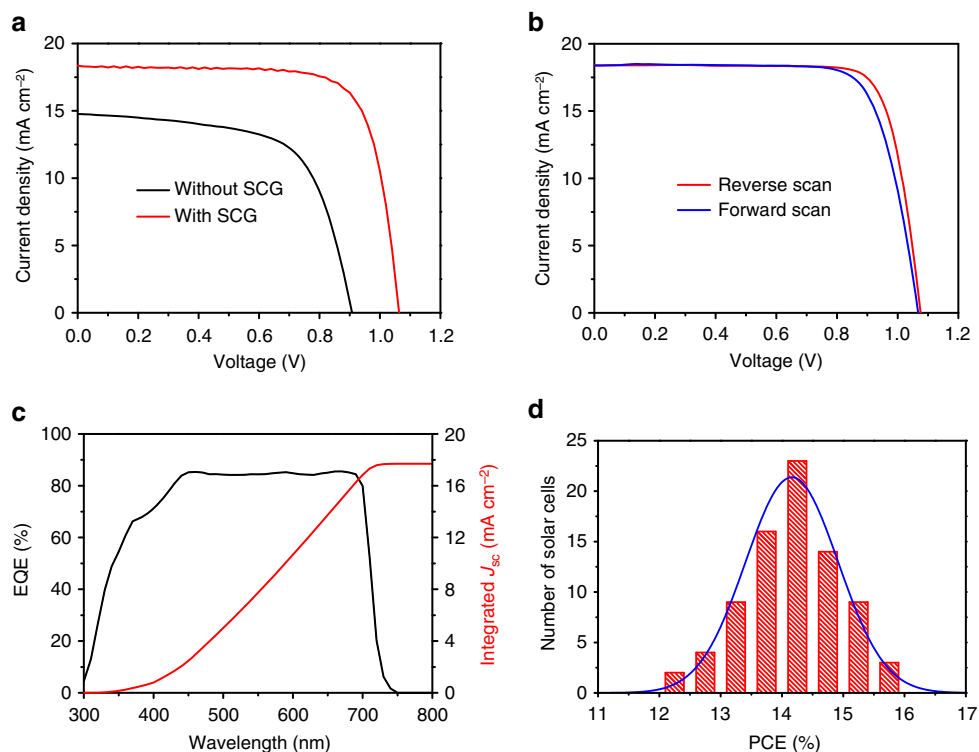


Fig. 3 Device performance of CsPbI₃-based solar cells. **a** *J*–*V* curves of the devices using CsPbI₃ as the absorber layer, while the CsPbI₃ without and with solvent-controlled growth (SCG), the SCG time is 50 min. **b** The device performance under forward scan (0 to 1.2 V) and reverse scan (1.2 to 0 V) for the best performance device. **c** External quantum efficiency (EQE) spectrum of a CsPbI₃ solar cell (black) and the integrated short-circuit current density (red). **d** Device performance distribution for 80 devices, the curve represents the Gaussian function of the histogram

pinholes (Fig. 1f). The morphology evolution dependent on the SCG times can be found in Supplementary Fig. 4. The significant improvement in perovskite films morphology indicated that SCG process is in favor of obtaining high-quality perovskite films.

Stability of the α -phase CsPbI₃ film in a dry environment. We carried out the XRD measurement for the annealed CsPbI₃ films. We found that α -phase CsPbI₃ crystal was formed by two steps from the precursor films with SCG. For the precursor film with SCG, the δ -phase and β -phase of CsPbI₃ coexisted at room temperature, and then was completely changed to δ -phase CsPbI₃ after annealing at 150 °C. After that, the precursor film was completely converted into α -phase CsPbI₃, while the temperature was increased to 350 °C (Supplementary Fig. 2a). Encouragingly, we found that the high quality of α -phase CsPbI₃ that we obtained via SCG method can be maintained in dry nitrogen environment for a long time, and there is no change in the XRD patterns or absorption spectra after 7 days of storage (Fig. 2a, b). And furthermore, the films were not degraded even after more than 2 months of storage in a dry environment (Fig. 2c), indicating that the dry environment can freeze the α -phase of CsPbI₃²⁵. Consistent with the previous reports^{25, 34, 35}, we also found the induction of phase changes from black to yellowish-white after exposing the films to ambient air with high humidity (Supplementary Fig. 5). Our results showed that the α -phase of CsPbI₃ can be maintained at room temperature if we can completely avoid moisture, and additional additives were not needed for phase stabilization^{25, 40, 41, 43–45}. Therefore, we can absolutely achieve stable CsPbI₃-based solar cells if we can completely avoid moisture.

Characterizations of CsPbI₃ film. We found that the photoluminescence (PL) emission peaks of CsPbI₃ were blue-shifted from 710 to 703 nm after SCG for 50 min (Supplementary Fig. 6), this could be due to the reduction of defect-related traps, while

the film quality was improved⁵¹. We tested the time-resolved photoluminescence (TRPL) of the CsPbI₃ films, the lifetime of CsPbI₃ was increased from 0.6 to 5.2 ns after SCG for 50 min (Supplementary Fig. 6), further confirming that the traps have been reduced after SCG of the perovskite layer. We also found that the PL of CsPbI₃ was improved gradually with increasing SCG time (Supplementary Fig. 6). The lifetime of SCG CsPbI₃ films is in few nanoseconds, which is still shorter than that of organic–inorganic hybrid perovskite with the lifetime in microseconds^{52, 53}, this could be further improved in future.

We characterized the chemical states and also the band structure of CsPbI₃ film, the full spectrum of X-ray photoelectron spectroscopy (XPS) and core energy-level spectra confirming the inclusion of Cs, Pb, and I element (Supplementary Fig. 7). And ultraviolet photoelectron spectroscopy (UPS) measurement was also carried out to determine the band structure of CsPbI₃. It could be estimated that the conduction band and valence band of CsPbI₃ are about 3.95 eV and 5.68 eV, respectively (Supplementary Fig. 8).

CsPbI₃-based solar cells and device performance. We adopted the high-quality SCG-CsPbI₃ perovskite films as the absorption layer to configure solar cells with the structure of Indium tin oxide (ITO)/SnO₂/CsPbI₃/Spiro-OMeTAD/Au. N-type of SnO₂ was used as the electron transport layer, which was confirmed as an excellent electron transport layer in organic–inorganic perovskite solar cells (Supplementary Fig. 9)¹⁰, and Spiro-OMeTAD was used as the hole transport layer. A cross-sectional scanning electron microscopy (SEM) image of the completed device is shown in Supplementary Fig. 10. It was found that there is no obvious grain boundary for CsPbI₃ in about 3 μ m scale. From the SEM image, it can be also estimated that the thicknesses of the SnO₂, perovskite layer, Spiro-OMeTAD, and Au are about 25 nm, 350 nm, 170 nm, and 60 nm, respectively.

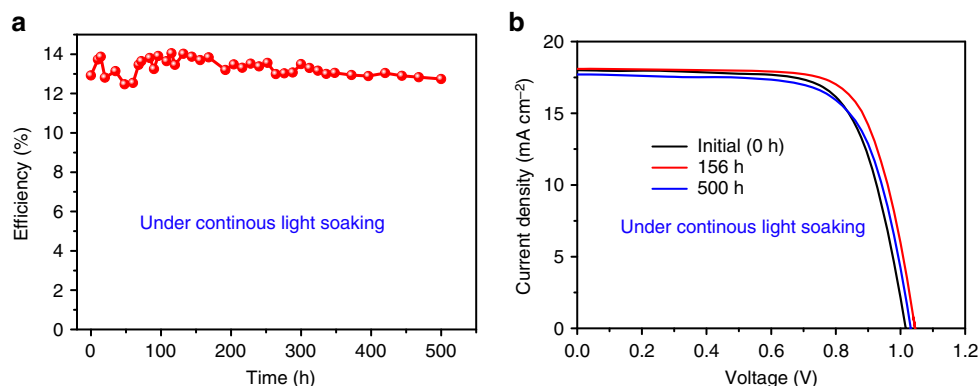


Fig. 4 Photostability of the CsPbI₃ solar cells. **a** Photostability measurement of the devices under continuous one-sun illumination (100 mW cm⁻²) with UV cut filter (420 nm) in nitrogen glove box (temperature: approximately 25 °C) for the unencapsulated devices. **b** *J*-*V* curve of the devices under different continuous light-soaking time

The device performance for the CsPbI₃ films with and without SCG was characterized (Fig. 3a, Supplementary Fig. 11). Specifically, when the perovskite layer is without SCG, the devices showed poor performance, with open circuit voltage (V_{OC}) of 0.91 V, short-circuit current density (J_{SC}) of 14.77 mA cm⁻², fill factor (FF) of 64%, and the efficiency of only 8.58%. The lower performance might be due to too many pinholes in the perovskite layer and lead to serious leakage and recombination⁴⁶. While SCG were carried out, the device performance enhanced significantly (Fig. 3a, Supplementary Fig. 11 and Supplementary Table 1). The best performance of 15.71% was obtained when the perovskite layer with optimized SCG time for 50 min, with the V_{OC} of 1.08 V, J_{SC} of 18.41 mA cm⁻², and FF of 79.32% (Fig. 3b, reverse scan). The efficiency we achieved here represents a great improvement compared with the previous reports in CsPbI₃-based solar cells (Supplementary Table 2). We tested the device performance under reverse and forward scan, the *J*-*V* curves show no appreciable hysteresis between the two different scan directions (Fig. 3b). Reverse and forward scans showed the efficiency of 15.71% and 14.93%, respectively, the average efficiency is about 15.32% (Fig. 3b). The typical external quantum efficiency (EQE) of the CsPbI₃ solar cells was given (Fig. 3c); the photoresponse edge is about 720 nm, corresponding to the bandgap of CsPbI₃ (1.73 eV). In the visible region, the EQE can reach up to 85% with an integrated short-circuit current of 17.7 mA cm⁻², which is almost consistent with the *J*-*V* result (Fig. 3a, b). Our devices also showed good reproducibility, the efficiency is located from 12.3 to 15.7% for 80 devices, and most of the PCEs are about 14% (Fig. 3d).

We encapsulated the best devices and sent them to photovoltaic calibration laboratory (Newport, an accredited PV calibration laboratory, USA) for certification, which confirmed that a stabilized PCE is 14.67%, the V_{OC} is 1.097 V, J_{SC} is 18.0 mA cm⁻², and FF is 74% (Supplementary Figs. 12 and 13). As we know, CsPbI₃ is very sensitive to moisture, the certified results showed that there is no significant degradation during shipping and measurements, while the encapsulated devices were completely exposed to ambient air with moisture for a long time (192 h), inferring that the phase stability issue of CsPbI₃ could be completely solved by encapsulation.

Device stability. The stability of perovskite solar cells is a critical issue^{22, 28, 54-61}, we tested the device's stability in the dark and also under continuous light soaking. We found that the device can almost keep its original efficiency when stored in dry nitrogen for 720 h (30 days) (Supplementary Fig. 14 and Supplementary

Table 3). More importantly, we found that our device showed excellent photostability under continuous light soaking in dry nitrogen environment. After 500 h of continuous light soaking (AM 1.5G, 100 mW cm⁻² with 420 nm UV light filter, temperature: approximately 25 °C), the device can maintain its original efficiency and no drop (Fig. 4a). As an example, the initial PCE of the device is 12.97%, after 156 h of continuous light soaking, the efficiency was slightly increased to 13.7%, which could be due to the improvement of the contact, and then dropped a little to 12.74% after 500 h of light soaking (Fig. 4b, Supplementary Table 4). The good photostability of CsPbI₃ solar cells could be due to the excellent thermal stability or large ion migration barrier of the inorganic perovskite materials³⁷. Longer-time photostability measurements are also carried out. Further improvement of the CsPbI₃-solar cells stability could be by doping of the perovskite layer^{34, 43, 58}, interface engineering^{55-57, 59, 60}, and also advanced encapsulation⁶¹.

Discussion

We found that our SCG method could be extended to obtain high-quality CsPbI₂Br films (Supplementary Fig. 15). According to SCG, a 14.21% PCE of CsPbI₂Br solar cells has been obtained (Supplementary Fig. 16 and Supplementary Table 5). Using this SCG method, we have also achieved as high as 16.14% and 9.81% PCE of CsPb(I_{0.85}Br_{0.15})₃- and CsPbBr₃-based solar cells, respectively (Supplementary Fig. 17). These results indicated that our SCG method is universal at least for high-quality inorganic perovskite films growth and also for obtaining efficient solar cells.

In conclusion, a 15.7% PCE of CsPbI₃ solar cells have been achieved by SCG of the absorb layer, and the devices can tolerate above 500 h of continuous light soaking. There is still a large room for device performance, especially on the open-circuit voltage, considering the bandgap of CsPbI₃ (1.73 eV); a 1.3 V open-circuit voltage should be feasible for CsPbI₃ solar cells if the contact and the defect can be perfectly controlled, and the efficiency will be close to or beyond 20%.

Methods

Materials. SnO₂-colloid precursor (tin(IV) oxide, 15% in H₂O colloidal dispersion), DMF, and DMSO were purchased from Alfa Aesar. CsI and PbI₂ were purchased from Sigma Aldrich.

Device fabrication. The ITO-coated transparent conducting substrate was successively washed with detergent solution, distilled water, acetone, and isopropanol, respectively. The CsPbI₃-precursor solution is made by dissolving CsI and PbI₂ (molar ratio 1:1) in a mixture of DMF and DMSO (v/v, 4:1). A compact 25-nm thin SnO₂ layer was spin-coated on the glass/ITO substrates, the details could be found elsewhere¹⁰. And then, the 0.8 M CsPbI₃-precursor solution was deposited by a

one-step spin-coating process onto the transport layer at the speed of 1500 rpm for 45 s. Other compositions of inorganic perovskite films were also used for fabrication of devices to show that our SCG method is a universal approach. For CsPbI₂Br solution, 0.8 M CsI mixed with 0.4 M PbI₂ and 0.4 M PbBr₂ were dissolved in DMF and DMSO solvent. For CsPb(I_{0.85}Br_{0.15})₃ solution, 0.85 M CsPbI₃ and 0.15 M CsPbBr₃ were mixed. For CsPbBr₃ solution, 0.4 M of CsBr:PbBr₂ (1:1) was dissolved in DMF and DMSO solvent. For SCG of the perovskite layer, we dried the fresh spin-coated perovskite precursor films in a glove box, ranging from 0 to 50 min. After drying, the precursor films were annealed at 350 °C for 10 min in nitrogen glove box for the formation of α -phase CsPbI₃ (the annealing temperature of CsPbBr₃ is 250 °C). For conventional growth without SCG, after spin-coating of perovskite precursor films, annealing was carried out immediately. After cooling of the annealed perovskite films, the Spiro-OMeTAD hole transport layer was applied by spin-coating at 2500 rpm for 30 s. A total of 1 mL of Spiro-OMeTAD/chlorobenzene solution contained 72.3 mg Spiro-OMeTAD with the addition of 35 μ L lithium bis(trifluoromethanesulfonyl)imide/acetoneitrile (260 mg mL⁻¹) and 30 μ L 4-tert-butylpyridine. Eventually, 60 nm of gold electrode was thermally evaporated on top of the device through a shadow mask, with an effective area of 0.108 cm².

Characterization. UV-vis spectra were carried out on a Varian Cary 5000 spectrophotometer. SEM measurements were measured with FEI NanoSEM650 to get the relevant parameters, including the morphology and composition of the films, additionally, also includes the device structures. The XRD patterns (θ -2 θ scans) were recorded with a Rigaku D/MAX-2500 system operated Cu K α ($\lambda = 1.5405$ Å) at 40 kV and 200 mA. Steady PL measurement was carried out by Nanolog TCSPC (USA), TRPL were carried out by Edinburgh Instruments F900 (UK). During XRD and PL measurement, to avoid degradation of the films, the films were spin-coated with PMMA for protection, the concentration of the PMMA solution was 8% in chlorobenzene, and the spin rate was 2000 rpm. UPS measurements were conducted on a Thermo Scientific ESCALab 250Xi using HeI (21.22 eV) radiation lines. XPS were also carried out on the Thermo Scientific ESCALab 250Xi with 200 W monochromated Al K α (1486.6 eV) radiation, and the XPS analysis using a 500 μ m X-ray spot. Current-voltage characteristics of the photovoltaic devices were measured with a Keithley 2400 source meter under a simulated AM 1.5G spectrum and a solar simulator (Enli Tech, Taiwan), before each measurement, the solar simulator was calibrated with a Si solar cell (KG-5). The I - V measurements were carried out in nitrogen glove box. The devices are both measured in reverse scan (1.2 to 0 V, step 0.02 V) and forward scan (0 to 1.2 V, step 0.02 V), the photovoltaic devices were measured in both forward scan and reverse scan at a scan rate of 0.02 V s⁻¹. The devices were taken out for EQE measurement, the EQE were measured by Enli Tech (Taiwan) EQE measurement system. Devices were encapsulated by the UV-epoxy and use-edge encapsulation method. For our best devices, we encapsulated the devices and then sent to PV calibration laboratory (Newport, an accredited PV calibration laboratory, USA) for certification, and during testing, a metal mask with the size of 0.0738 cm² has been used. For shelf-stability test, we stored the solar cells in nitrogen glove box and measured it intermittently, and we collected the shelf-stability in 720 h. For the photostability test, the devices were soaked under continuous one-sun condition with UV cut filter (AM 1.5G, 100 mW cm⁻², 420 nm cut filter), the J - V curves were collected every several hours, and we collected the device's photostability in 500 h. The photostability test was also carried out in nitrogen glove box for the device without encapsulation.

Data availability. The data that support the findings of this study are available from the corresponding author upon reasonable request.

Received: 11 February 2018 Accepted: 17 April 2018

Published online: 08 June 2018

References

- Kojima, A., Teshima, K., Shirai, Y. & Miyasaka, T. Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. *J. Am. Chem. Soc.* **131**, 6050–6051 (2009).
- Kim, H.-S. et al. Lead iodide perovskite sensitized all-solid-state submicron thin film mesoscopic solar cell with efficiency exceeding 9%. *Sci. Rep.* **2**, 591 (2012).
- Lee, M. M., Teuscher, J., Miyasaka, T., Murakami, T. N. & Snaith, H. J. Efficient hybrid solar cells based on meso-structured organometal halide perovskites. *Science* **338**, 643–647 (2012).
- Zhou, H. et al. Interface engineering of highly efficient perovskite solar cells. *Science* **345**, 542–546 (2014).
- Yang, W. S. et al. High-performance photovoltaic perovskite layers fabricated through intramolecular exchange. *Science* **348**, 1234–1237 (2015).
- Nie, W. et al. High-efficiency solution-processed perovskite solar cells with millimeter-scale grains. *Science* **347**, 522–525 (2015).
- Jeon, N. J. et al. Compositional engineering of perovskite materials for high-performance solar cells. *Nature* **517**, 476–480 (2015).
- Son, D. Y. et al. Self-formed grain boundary healing layer for highly efficient CH₃NH₃PbI₃ perovskite solar cells. *Nat. Energy* **1**, 16081 (2016).
- Bi, D. et al. Polymer-templated nucleation and crystal growth of perovskite films for solar cells with efficiency greater than 21%. *Nat. Energy* **1**, 16142 (2016).
- Jiang, Q. et al. Enhanced electron extraction using SnO₂ for high-efficiency planar-structure HC(NH₂)₂PbI₃-based perovskite solar cells. *Nat. Energy* **2**, 16177 (2016).
- Tan, H. et al. Efficient and stable solution-processed planar perovskite solar cells via contact passivation. *Science* **355**, 722–726 (2017).
- Wu, Y. et al. Perovskite solar cells with 18.21% efficiency and area over 1 cm² fabricated by heterojunction engineering. *Nat. Energy* **1**, 16148 (2016).
- Zheng, X. et al. Defect passivation in hybrid perovskite solar cells using quaternary ammonium halide anions and cations. *Nat. Energy* **2**, 17102 (2017).
- Yang, W. S. et al. Iodide management in formamidinium-lead-halide-based perovskite layers for efficient solar cells. *Science* **356**, 1376–1379 (2017).
- Chen, H. et al. A solvent- and vacuum-free route to large-area perovskite films for efficient solar modules. *Nature* **550**, 92–95 (2017).
- Berhe, T. A. et al. Organometal halide perovskite solar cells: degradation and stability. *Energy Environ. Sci.* **9**, 323–356 (2016).
- Conings, B. et al. Intrinsic thermal instability of methylammonium lead trihalide perovskite. *Adv. Energy Mater.* **5**, 1500477 (2015).
- Kulbak, M. et al. Cesium enhances long-term stability of lead bromide perovskite-based solar cells. *J. Phys. Chem. Lett.* **7**, 167–172 (2016).
- Kulbak, M., Cahen, D. & Hodes, G. How important is the organic part of lead halide perovskite photovoltaic cells? Efficient CsPbBr₃ cells. *J. Phys. Chem. Lett.* **6**, 2452–2456 (2015).
- Lee, J. W. et al. Formamidinium and cesium hybridization for photo- and moisture-stable perovskite solar cell. *Adv. Energy Mater.* **5**, 1501310 (2015).
- Saliba, M. et al. Cesium-containing triple cation perovskite solar cells: improved stability, reproducibility and high efficiency. *Energy Environ. Sci.* **9**, 1989–1997 (2016).
- Saliba, M. et al. Incorporation of rubidium cations into perovskite solar cells improves photovoltaic performance. *Science* **354**, 206–209 (2016).
- Li, Z., Yang, M., Park, J.-S., Wei, S.-H., Berry, J. J. & Zhu, K. Stabilizing perovskite structures by tuning tolerance factor: formation of formamidinium and cesium lead iodide solid-state alloys. *Chem. Mater.* **28**, 284–292 (2016).
- Eperon, G. E. et al. Formamidinium lead trihalide: a broadly tunable perovskite for efficient planar heterojunction solar cells. *Energy Environ. Sci.* **7**, 982–988 (2014).
- Eperon, G. E. et al. Inorganic cesium lead iodide perovskite solar cells. *J. Mater. Chem. A* **3**, 19688–19695 (2015).
- Zhao, D. et al. Low-bandgap mixed tin-lead iodide perovskite absorbers with long carrier lifetimes for all-perovskite tandem solar cells. *Nat. Energy* **2**, 17018 (2017).
- McMeekin, D. P. et al. A mixed-cation lead mixed-halide perovskite absorber for tandem solar cells. *Science* **351**, 151–155 (2016).
- Bush, K. A. et al. 23.6%-efficient monolithic perovskite/silicon tandem solar cells with improved stability. *Nat. Energy* **2**, 17009 (2017).
- Eperon, G. E. et al. Perovskite-perovskite tandem photovoltaics with optimized bandgaps. *Science* **354**, 861–865 (2016).
- Ahmad, W., Khan, J., Niu, G. & Tang, J. Inorganic CsPbI₃ perovskite-based solar cells: a choice for a tandem device. *Sol. RRL* **1**, 1700048 (2017).
- Stoumpos, C. C., Malliakas, C. D. & Kanatzidis, M. G. Semiconducting tin and lead iodide perovskites with organic cations: phase transitions, high mobilities, and near-infrared photoluminescent properties. *Inorg. Chem.* **52**, 9019–9038 (2013).
- Dastidar, S. et al. High chloride doping levels stabilize the perovskite phase of cesium lead iodide. *Nano Lett.* **16**, 3563–3570 (2016).
- Lin, J. et al. Thermochromic halide perovskite solar cells. *Nat. Mater.* **17**, 261–267 (2018).
- Beal, R. E. et al. Cesium lead halide perovskites with improved stability for tandem solar cells. *J. Phys. Chem. Lett.* **7**, 746–751 (2016).
- Sutton, R. J. et al. Bandgap-tunable cesium lead halide perovskites with high thermal stability for efficient solar cells. *Adv. Energy Mater.* **6**, 1502458 (2016).
- Lau, C. F. J. et al. CsPbI₂Br₂ perovskite solar cell by spray-assisted deposition. *ACS Energy Lett.* **1**, 573–577 (2016).
- Zhou, W. et al. Light-independent ionic transport in inorganic perovskite and ultrastable Cs-based perovskite solar cells. *J. Phys. Chem. Lett.* **8**, 4122–4128 (2017).
- Frolova, L. A. et al. Highly efficient all-inorganic planar heterojunction perovskite solar cells produced by thermal coevaporation of CsI and PbI₂. *J. Phys. Chem. Lett.* **8**, 67–72 (2016).
- Chen, C. Y. et al. All-vacuum-deposited stoichiometrically balanced inorganic cesium lead halide perovskite solar cells with stabilized efficiency exceeding 11%. *Adv. Mater.* **29**, 1605290 (2017).

40. Wang, Q., Zheng, X., Deng, Y., Zhao, J., Chen, Z. & Huang, J. Stabilizing the α -phase of CsPbI₃ perovskite by sulfobetaine zwitterions in one-step spin-coating films. *Joule* **1**, 1–12 (2017).
41. Luo, P. et al. Solvent engineering for ambient-air-processed, phase-stable CsPbI₃ in perovskite solar cells. *J. Phys. Chem. Lett.* **7**, 3603–3608 (2016).
42. Swarnkar, A. et al. Quantum dot-induced phase stabilization of CsPbI₃ perovskite for high-efficiency photovoltaics. *Science* **354**, 92–95 (2016).
43. Hu, Y. et al. Bismuth incorporation stabilized α -CsPbI₃ for fully inorganic perovskite solar cells. *ACS Energy Lett.* **2**, 2219–2227 (2017).
44. Zhang, T. et al. Bication lead iodide 2D perovskite component to stabilize inorganic α -CsPbI₃ perovskite phase for high-efficiency solar cells. *Sci. Adv.* **3**, e1700841 (2017).
45. Sanehira, E. M. et al. Enhanced mobility CsPbI₃ quantum dot arrays for record-efficiency, high-voltage photovoltaic cells. *Sci. Adv.* **3**, ea04204 (2017).
46. Eperon, G. E. et al. Morphological control for high performance, solution-processed planar heterojunction perovskite solar cells. *Adv. Funct. Mater.* **24**, 151–157 (2014).
47. Jeon, N. J. et al. Solvent engineering for high-performance inorganic–organic hybrid perovskite solar cells. *Nat. Mater.* **13**, 897–903 (2014).
48. You, J. et al. Moisture assisted perovskite film growth for high performance solar cells. *Appl. Phys. Lett.* **105**, 183902 (2014).
49. Fu, Y. et al. Selective stabilization and photophysical properties of metastable perovskite polymorphs of CsPbI₃ in thin films. *Chem. Mater.* **29**, 8385–8394 (2017).
50. Li, G. et al. High-efficiency solution processable polymer photovoltaic cells by self-organization of polymer blends. *Nat. Mater.* **4**, 864–865 (2015).
51. Shao, Y., Xiao, Z., Bi, C., Yuan, Y. & Huang, J. Origin and elimination of photocurrent hysteresis by fullerene passivation in CH₃NH₃PbI₃ planar heterojunction solar cells. *Nat. Commun.* **5**, 5784 (2014).
52. Stranks, S. D. et al. Electron-hole diffusion lengths exceeding 1 micrometer in an organometal trihalide perovskite absorber. *Science* **342**, 341–344 (2013).
53. deQuilettes, D. W. et al. Impact of microstructure on local carrier lifetime in perovskite solar cells. *Science* **348**, 683–686 (2015).
54. Yang, Y. & You, J. Make perovskite solar cells stable. *Nature* **544**, 155–156 (2017).
55. Mei, A. et al. A hole-conductor-free, fully printable mesoscopic perovskite solar cell with high stability. *Science* **345**, 295–298 (2014).
56. Chen, W. et al. Efficient and stable large-area perovskite solar cells with inorganic charge extraction layers. *Science* **350**, 944–948 (2016).
57. Shin, S. S. et al. Colloidally prepared La-doped BaSnO₃ electrodes for efficient, photostable perovskite solar cells. *Science* **356**, 167–171 (2017).
58. Nam, J. K. et al. Potassium incorporation for enhanced performance and stability of fully inorganic cesium lead halide perovskite solar cells. *Nano Lett.* **17**, 2028–2033 (2017).
59. Arora, N. et al. Perovskite solar cells with CuSCN hole extraction layers yield stabilized efficiencies greater than 20%. *Science* **358**, 768–771 (2017).
60. Hou, Y. et al. A generic interface to reduce the efficiency-stability-cost gap of perovskite solar cells. *Science* **358**, 1192–1197 (2017).
61. Bella, F. et al. Improving efficiency and stability of perovskite solar cells with photocurable fluoropolymers. *Science* **354**, 203–206 (2016).

Acknowledgments

This work was supported by National Key Research and Development Program of China (Grant No. 2016YFB0700700), National Natural Science Foundation of China (Grant Numbers: 61634001, 61574133), Beijing Municipal Science & Technology Commission (Grant No. Z181100004718005), National 1000 Young Talents awards and also was partially supported by Hanergy group.

Author contributions

J.Y. conceived the idea, directed, and supervised the project. P.W. fabricated the devices and collected all the data. X.Z., Y.Z., Q.J., Q.Y., X.L., X.Y., Z.C., and Z.Y. were involved in data analysis. J.Y. and P.W. co-wrote the manuscript. All authors contributed to the discussions and finalizing of the manuscript.

Additional information

Supplementary Information accompanies this paper at <https://doi.org/10.1038/s41467-018-04636-4>.

Competing interests: The authors declare no competing interests.

Reprints and permission information is available online at <http://npg.nature.com/reprintsandpermissions/>

Publisher's note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Open Access This article is licensed under a Creative Commons

Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>.

© The Author(s) 2018