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Constructing "hillocks"-like random-textured absorber for efficient planar perovskite solar cells



Lin Fan^{a,b,d}, Pengfei Wang^a, Shuo Yang^c, Lili Yang^{a,b,*}, Fengyou Wang^{a,b}, Xiaoyan Liu^{a,b}, Maobin Wei^{a,b}, Huilian Liu^{a,b}, Yingrui Sui^{a,b}, Federico Rosei^e, Jinghai Yang^{a,b,*}

^a Key Laboratory of Functional Materials Physics and Chemistry of the Ministry of Education, Jilin Normal University, Changchun 130103, China

^b National Demonstration Center for Experimental Physics Education, Jilin Normal University, Siping 136000, China

^c Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China

^d Key Laboratory of Preparation and Application of Environmental Friendly Materials, Ministry of Education, Jilin Normal University, Changchun 130103, China

e Center for Energy, Materials and Telecommunications, Institut National de La Recherche Scientifque, 1650 Boulevard Lionel-Boulet, Varennes J3X 1S2, Quebec, Canada

HIGHLIGHTS

- We developed a "hillocks"-like random-textured perovskite (HRT-perovskite) absorber.
- Crystallization kinetics and formation mechanisms of CB-induced HRT-perovskite absorbers have been proposed.
- Proper volume CB promoted the construction of porous MAI-PbI₂-DMSO intermediate structure.
- Efficient light trapping was achieved by employing CB-induced HRT-perovskite absorbers.

ARTICLE INFO

Keywords: Planar perovskite solar cells Textured absorbers Light harvesting Anti-solvent Intermediate phase

G R A P H I C A L A B S T R A C T



ABSTRACT

Efficient planar heterojunction perovskite solar cells (PSCs) with high-quality absorbers are promising for flexible-, semitransparent-, and tandem- photovoltaic applications. However, compared to mesoporous PSCs, planar perovskite absorbers tend to suffer from additional optical losses due to insufficient light harvesting. Accordingly, the design and fabrication of high-quality textured perovskite absorbers are promising to improve device performance. We developed a "hillocks"-like random-textured perovskite (HRT-perovskite) absorber using a facile chlorobenzene (CB) anti-solvent assisted spin-coating approach. The crystallization kinetics and formation mechanisms of CB-induced HRT-perovskite absorbers have been systematically explored, allowing us to gain insights into the role of CB, i.e. an appropriate volume of CB promotes the formation of a porous MAI-PbI₂-DMSO intermediate structure. We show that the porous nature of the intermediate film provides sufficient space for lattice reconstruction and structure expansion during crystal growth, thus effectively improving the film and surface/interface quality, and, ultimately, the optoelectronic properties of the perovskite absorber. Moreover, the HRT-perovskite absorber exhibits excellent light-trapping capability and carrier mobility, due to its optimized surface roughness and longitudinally ordered grain boundary distribution. As a result, we obtained efficiencies of up to 20.03% from planar heterojunction PSCs fabricated using ~400 nm thick HRT-perovskite absorbers. The process exhibits very high reproducibility with 20 individual devices fabricated in one batch, achieving an average power conversion efficiency (PCE) of 19.00%. Finally, the whole fabrication process was conducted below 150 °C, which is appropriate for a wide range of applications, such as flexible- and tandem- photovoltaic devices.

* Corresponding authors. *E-mail addresses*: llyang1980@126.com (L. Yang), jhyang1@jlnu.edu.cn (J. Yang).

https://doi.org/10.1016/j.cej.2020.124091

Received 5 November 2019; Received in revised form 7 January 2020; Accepted 10 January 2020 Available online 11 January 2020 1385-8947/ © 2020 Elsevier B.V. All rights reserved.

1. Introduction

Hybrid metal halide perovskite solar cells (PSCs) are considered as the most promising for next-generation photovoltaic technologies, mostly due to their remarkable development speed, excellent power conversion efficiencies (PCEs), and low-cost processability [1-6]. Regardless of the device configuration, the superior optoelectronic properties of hybrid perovskite materials underpin the high values of PCE [7–9]. Methylammonium lead iodide perovskite (CH₃NH₃PbI₃, MAPbI₃) has been commonly used as light absorber, due to its simple crystal structure and appropriate optical band gap (1.51-1.61 eV) [10,11]. In recent years, various synthesis techniques have been used to fabricate high-quality MAPbI₃ absorbers and high-efficiency devices. such as one- or two-step sequential spin-coating deposition and chemical vapor evaporation [12-15]. The one-step anti-solvent assisted method firstly reported by Cheng and co-workers has proven to be the most efficient approach for improving the crystallization, surface/interface morphology and optoelectronic properties of MAPbI₃ absorbers [13,16,17]. When an anti-solvent with a low dipole moment and dielectric constant, typically chlorobenzene (CB), is introduced into the initial solution, the initial solvent would be partially extracted by the newly added anti-solvent, so the concentration of solute in the initial solution is raised to supersaturation in an extremely short time, thus promoting the precipitation and crystallization of the solute [18,19]. Through various phases of optimization, the PCEs of MAPbI₃-based PSCs prepared by anti-solvent precipitation increased from ~13% to over 21% [13,20,21].

Despite these record efficiencies, a large portion of the incident light is still lost without contributing to the PCE, especially in planar heterojunction devices with relatively thin MAPbI₃ absorbers, resulting in the theoretical maximum short-circuit current density (J_{SC}) of MAPbI₃based PSCs ($\sim 26 \text{ mA cm}^{-2}$) not yet being achieved [22]. Accordingly, a variety of strategies have been developed to compensate the optical losses, such as using anti-reflective layers on the light-incident side [23,24], introducing scattering media [25,26], and/or depositing textured charge transporting layers or perovskite absorbers [8,9,27-30]. However, the highly textured substrates easily induce a high density of micro-voids in the perovskite absorbers, which act as recombination centers and deteriorate device performance [31]. The deposition of high-quality textured perovskite absorbers is regarded as an effective way to reduce photoelectric loss, which can promote charge separation/extraction by increasing the interface area between the perovskite and the adjacent contacts, thus increasing J_{SC} and the PCE of PSCs [8,9,27,28]. Meanwhile, from the perspective of device configuration, when these random-textured absorbers are combined with metal rear electrodes in solar cells, they can effectively extend the length of the reflected light path and improve the light-harvesting efficiency (i.e., the incident light passing through the absorber is reflected back into the perovskite for re-absorption). Thus, this technology is more effective compared to other light-trapping strategies [32,33].

In recent years, Cao et al. introduced MACl into the pristine MAPbI₃ precursor for anti-solvent precipitation, and fabricated high-quality random-textured MAPbI₃ films, which effectively improved the light harvesting and interfacial charge extraction of the planar devices [34]. Subsequently, Song et al. [35] and Ho et al. [8] constructed "whispering-gallery"-like and "coral"-like MAPbI₃ absorbers by using reformed anti-solvent assisted spin-coating methods (i.e., surface imprinting and surface modification), respectively. Ultimately, the efficiency of planar MAPbI₃-based PSC was increased to 19.80% with a $J_{\rm SC}$ of 23.62 mA cm⁻², a fill factor (*FF*) of 76.61% and an open-circuit voltage ($V_{\rm OC}$) of 1.09 V.

However, the tedious process, long time-consuming and additional additives are not conducive to the low-cost and repeatability of devices, so it is urgent to explore a low-cost and easy-to-control method for obtaining high-quality textured absorbers and efficient devices. Here, we used a typical and simple CB anti-solvent assisted method to construct a novel "hillocks"-like random-textured perovskite (HRTperovskite, HRT-MAPbI₃) absorber. The effect of the CB dipping amount on the morphology and intermediate-phase crystallization kinetics of the perovskite was systematically studied, revealing that an optimal CB volume promotes the formation of a porous intermediate structure, which provides sufficient space for subsequent grain growth, thus significantly improving absorber quality, grain boundary distribution, light-harvesting capability and charge separation/collection efficiency. Through the structure design of HRT-perovskite, the planar heterojunction PSC (~400 nm-thick HRT-MAPbI₃ absorber) efficiency was enhanced to 20.03% with a J_{SC} of 22.98 mA cm⁻², a FF of 77.53% and a $V_{\rm OC}$ of 1.12 V. This technique also exhibits very high reproducibility and achieves an average PCE of 19.00%. Additionally, all processes were conducted at a relatively low temperature (≤ 150 °C), which is desirable for a wide range of applications, such as flexible- and tandem- solar cells on thermal-sensitive substrates. Table 1 summaries the key fabrication techniques and planar device performance parameters employing textured perovskite absorbers reported previously, as well as how our results outperform those of previous studies [8,9,27,28,34-37].

2. Experimental section

2.1. Materials

Etched indium-doped tin oxide (ITO) conducting glass substrates were purchased from Yingkou Optimum Trade Co., Ltd., while SnO₂ colloidal dispersion (SnO₂ 15% in H₂O colloidal dispersion), dimethyl sulfoxide (DMSO, \geq 99.8%) and dimethylformide (DMF, \geq 99.8%) were purchased from Alfa Aesar. Lead iodide (Pbl₂, 99.999%) and methylammonium iodide (CH₃NH₃I, MAI) were obtained from Sigma-Aldrich, while chlorobenzene (CB) was purchased from Aladdin Reagents. The organic hole transporting materials, Spiro-OMeTAD (2,2',7,7'-Tetrakis [N,N-di(4-meth-oxyphenyl)amino]-9,9'-spirobifluorene), sulfonyl imide (Li-TFSI) and *tert*-butylpyridine (TBP) were purchased from Yingkou Optimum Trade Co., Ltd.

All reagents were of analytical grade and used without further purification. The purity of the silver (Ag) used for thermally evaporated electrode was 99.99%.

2.2. Solar cells fabrication

The etched ITO substrates were ultrasonically washed with acetone, deionized water, and ethanol sequentially for 15 min. The cleaned ITO-coated substrates were dried at 80 °C for 12 h followed by treatment with UV-ozone for 30 min. Compact SnO_2 electron transporting layers (ETLs) were prepared by spin-coating aqueous solutions of SnO_2 onto the ITO substrates at 5000 r.p.m. for 30 s, and subsequently heated in air at 150 °C for 30 min. The average thickness of the compact SnO_2 substrates were immediately transferred into a nitrogen-filled glove box for perovskite absorber and hole transporting layer (HTL) preparation.

All perovskite films were fabricated by using a simple anti-solventassisted spin-coating method previously reported in the literature [17]. A mixture solution of 1 M PbI₂/MAI (with a molar ratio of 1:1), dissolved in a DMSO and DMF mixed solvent (3:7 vol ratio), was spincoated onto the compact SnO₂ ETLs at 500 r.p.m. for 13 s and 3500 r.p.m. for 37 s. During the second spin-coating stage, the substrates were treated with different volumes of CB solution. After drying at 60 °C and 110 °C for 5 min and 10 min, respectively, the as-prepared perovskite absorbers were obtained for fabricating solar cells.

An organic HTL solution was prepared by dissolving Spiro-OMeTAD (0.08 g), Li-TFSI (17.5 μ L) solution (0.52 g Li-TFSI in 1 mL acetonitrile) and TBP (28.5 μ L) in 1 mL of acetonitrile and CB (1:10, v/v), which was spin-coated onto the ITO/SnO₂/MAPbI₃ substrates at 5000 r.p.m. for 13 s and 6000 r.p.m. for 37 s to form a ~200 nm-thick dense Spiro-

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Preparation processes		Structures		Performance	e parameters			Ref.
Methods	Treatments	Perovskites	Devices	$J_{ m SC}$ (mA cm ⁻²)	FF (%)	V _{oc} (V)	Eff. (%)	
One-step anti-solvent assisted spin-coating method (Anti-solvent: ethyl acetate)	Addition of MACl to MAPbI ₃ precursor	Textured MAPbI ₃ films (Single-layer structure)	Planar	21.87	75.00	1.06	17.22	[34]
MA partial pressure controlmethod	Low partial pressure treatment of HPbI ₃ film by MA gas	Textured MAPbI ₃ films (Single-layer structure)	Planar	22.60	76.1	1.10	18.90	[6]
Two-step spin coating method	Perovskite random nano-texturing is transferred to the back semiconductor/metal interface	Textured perovskitefilms (Single-layer structure)	Planar	22.7	78.6	1.08	19.3	[36]
One-step anti-solvent assisted spin-coating method (Anti-solvent: toluene)	Surface-imprinted method	Micro-scale Whispering-gallery structured MAPbI ₃ films (Bilayer structure)	Planar	23.62	76.61	1.09	19.80	[35]
One-step anti-solvent assisted spin-coating method (Anti-solvent: CB)	Surface modification (Co-solvents: FAI/DMF/IPA)	Coral-like Perovskite films (Bilayer structure)	Planar	23.82 (AVG)	72.00 (AVG)	1.05 (AVG)	18.02 (AVG) 19.47 (MAX)	[8]
One-step anti-solvent assisted spin-coating method (Anti-solvent: CB)	Construction of porous intermediate by optimizing CB dipping amounts	HRT-MAPbI ₃ (Single-layer structure)	Planar	22.98	77.53	1.12	20.03	This work
One-stepgas-assisted spin-coating method	Addition of MACl to MAPbl ₃ precursor	Maze-like MAPbI ₃ film (Bilayer structure)	ETL-free	22.2	77.00	1.08	18.50	[37]
One-step gas-assisted spin-coating method	High-pressure nitrogen treatment	Textured MAPbI ₃ films (Multitiered nanostructure)	Mesoporous	22.31	71.30	1.02	16.33	[28]
One-step anti-solvent assisted spin-coating method (Anti-solvent: n-hexane)	N- hexane treatment	Ultrafast carrier extract architecture (UFCEA) MAPbI ₃ films (Bilayer structure)	Mesoporous	22.42	71.23	1.06	16.93	[27]

OMeTAD HTL. We used sufficient Spiro-OMeTAD drops (\sim 80 µL) to ensure the complete coverage of HTL.

Finally, a ~ 100 nm-thick Ag film was deposited by thermal evaporation as the top electrode. The active area (0.10 cm²) of the device was defined by using a shadow mask during Ag evaporation. It was not sealed but rather stored under dry conditions and characterized in normal ambient atmosphere.

2.3. Materials characterization and solar cell performance measurements

The surface and cross-sectional morphologies of the samples were characterized by Hitachi S-4800 scanning electron microscopy (SEM), respectively. The crystal structure of the samples was examined by X-ray diffraction (XRD, Rigaku, Japan) using Cu–K_a radiation as the radiation source ($\lambda = 0.15406$ nm) across a 2 θ range of 3° to 80°. Ultraviolet–visible (UV–vis) absorption spectra of perovskite films were recorded on a UV-3101PC spectrophotometer of SHIMADZU Japan. Fourier transform infrared spectroscopy (FTIR, Thermo Fisher IS50R, USA) was used to collect spectral data for the intermediate in the range of 4,200–600 cm⁻¹. The steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectroscopy were measured with the PL spectrometer (Fluorolog-3-TCSPC). The samples were excited by a pulsed laser, with a wavelength and frequency of 403 nm and 1 MHz. A band-pass filter at 655 nm was used to filter out the excitation light in the transient PL measurements.

The photocurrent dependence on the voltage (*J*–*V*) was measured at 25 °C under AM 1.5G simulated sunlight illumination (100 mW cm⁻², Model 91160, Orie). The spectral response of PSCs was taken by an external quantum efficiency (EQE) measurement system (QEX10, PV Measurement), equipped with a monochromator, a lock-in amplifier, a Xe lamp, and a current–voltage amplifier. The electrochemical impedance spectroscopy (EIS) of the devices was performed using an electrochemical workstation (CHI660C) at a voltage bias of 0.8 V in the absence of light.

3. Results and discussion

To explore the formation mechanism of HRT-perovskite absorbers. the morphological properties of the films before and after annealing were extensively analyzed. Fig. 1 depicts the detailed fabrication processes, and the anti-solvent-assisted spin-coating processes are described in the Section 2. A mixture of MAI, PbI₂, DMF and DMSO in an appropriate molar ratio was spread over the entire surface of the ITO/ SnO₂ substrate. Subsequently, the spin speed was accelerated to the desired value and maintained to evaporate polar solvents. After a specific delay time, different volumes of CB solution were quickly dropcasted onto the spinning substrates. During this anti-solvent treatment process, together with the removal of the residual polar solvents, all constituents precipitated into a uniform layer with a complex intermediate phase. We define the resulting films (i.e., unannealed colloidal films) as CB1-UCF (~250 µL), CB2-UCF (~350 µL), and CB3-UCF (~450 μ L). Finally, the complex was converted into a highly uniform perovskite after low-temperature annealing; meanwhile, the corresponding perovskite films with different CB dipping amounts are defined as CB1-PVK, CB2-PVK and CB3-PVK, respectively, in the following.

Top-view scanning electron microscopy (SEM) images of the UCFs



Fig. 1. Schematic diagram of fabrication processes of perovskite films treated with different CB dipping amounts.

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and corresponding perovskite films fabricated with different CB dipping amounts are shown in Fig. 2a and b, respectively. The intermediate mixtures are densely packed with very few voids in CB1-UCF (as shown in Fig. 2a-1). However, as the CB dipping amount increases, CB2-UCF becomes porous as visible in Fig. 2a-2, while CB3-UCF exhibits a dense surface as depicted in Fig. 2a-3. We speculate that the difference in morphology may be due to the different degrees of extraction and complexation of polar solvents caused by different CB dipping amounts. The appropriate CB amount (i.e., CB2 treatment) can fully extract polar solvents and rapidly form intermediate complexes, which would effectively coordinate the nucleation and crystallization rate, thus forming a pure UCF with a porous structure. Instead, an insufficient or excessive amount of CB would insufficiently or excessively extract polar solvents, respectively, resulting in a small amount of polar solvent (i.e., CB1 treatment) or anti-solvent (i.e., CB3 treatment) remaining in the intermediate complexes, thus disrupting the coordinated nucleation and growth rate, and eventually forming mixed UCFs.

After low-temperature annealing, the UCFs gradually transformed into perovskite films through intramolecular exchange between MAI and DMSO [38]. Compact and uniform CB2-PVK film with large grain "hillocks"-like random-textured structure has clearly been realized from the porous intermediate film, as shown in Fig. 2b-2 and Fig. 3. This is mainly attributed to the fact that the crystal structures of the intermediate complex and perovskite are totally different; as a result, the structural reconstruction and crystal expansion are likely to occur during annealing [14]. The porous nature of CB2-UCF can provide sufficient space for the structural expansion caused by the perovskite formation, thus effectively releasing stress and improving the grain size, film, and surface/interface properties [15]. In contrast, the compact and smooth CB1-UCF prohibits structure expansion, resulting in corresponding film with relatively small grain size and abundant grain boundaries, as shown in Fig. 2b-1. Similarly, the dense and large-grain CB3-UCF blocked the crystal's transverse growth, thus forming the CB3-PVK film with unavoidable structural defects and deformations, as shown in Fig. 2b-3.

The cross-sectional SEM images of the corresponding perovskite films and the schematics of their optical paths are depicted in Fig. 3. Incident light penetrates the perovskite absorber where it is partially or fully absorbed, depending on the thickness and wavelength of the perovskite film. In a PSC with a relatively flat rear interface, such incident light is mirror reflected, making a second pass in the CB1-PVK film during which it is further absorbed, before escaping the device through the front electrode (i.e., ITO-glass). However, in this configuration, the light absorption is inefficient at the spectral vicinity of the

perovskite band-gap, unless the film thickness is increased up to a few microns [36]. In a device based on a random-textured rear interface (such as CB2-PVK and CB3-PVK), the incident light not absorbed after one pass through the perovskite absorber is backscattered into it with a broad angular distribution, thus effectively extending the length of the optical path and improving the light-harvesting efficiency, which is conducive to the improvement of J_{SC} and PCE. However, although CB3-PVK has large grains and appropriate thickness, its abundant defects and poor ETL/CB3-PVK and CB3-PVK/HTL hetero-interface would lead to significant charge recombination and non-negligible optical loss, resulting in the reduction of FF, V_{OC} and J_{SC} . Fortunately, the HRTperovskite absorber (i.e., CB2-PVK) has appropriate roughness, larger grain size, unique light-scattering upper surface and longitudinally ordered grain boundary distribution, which enhances the surface area at the hetero-interface between the perovskite and Spiro-OMeTAD HTL and also promotes the photocurrent density and photo-generated charge separation/collection efficiency, thus contributing to the improvement of the overall PSC performance.

To illustrate the light-harvesting capability of the above perovskite films, we acquired ultraviolet–visible (UV–vis) absorption spectra (Fig. 4a). All the samples exhibit obvious absorption spectra at region of 400–800 nm and their absorption edges are similar to that of a classical MAPbI₃ perovskite, in agreement with previous reports [12,17]. The HRT-perovskite absorber (i.e., CB2-PVK) exhibits superior absorption compared to the other two films, which is beneficial for harvesting more light to generate more carriers and thus enhances the J_{SC} and PCE. However, the absorbance of the CB1-PVK film is the lowest between 400 and 800 nm, which is ascribed to significant loss of incident light. Similarly, the relatively low absorption of the CB3-PVK film is attributed to its poor crystallinity. These observations are consistent with the above SEM results.

The optical band gaps of perovskite films treated with different CB dipping amounts can be derived from absorption spectra and described by the following equation to calculate the band-gap energy (E_g) [39]:

$$\alpha h \nu = A (h \nu - E_g)^n \tag{1}$$

where α is the absorption coefficient, $h\nu$ is photon energy, A is a constant, and n varies according to allowed or forbidden direct and indirect transitions. The value n = 1/2 is employed in this case since the perovskite is regarded as a direct band-gap semiconductor. As a result, the average band gap of CB1-PVK, CB2-PVK and CB3-PVK is calculated to be 1.59 eV. The corresponding Tauc plots are presented in Fig. 4b.

To reveal the growth mechanism of the CB-induced high-quality HRT-perovskite absorber and the critical kinetic control strategy of



Fig. 2. The top-view SEM images of (a-1) the CB1-UCF, (a-2) the CB2-UCF, (a-3) the CB3-UCF, and corresponding perovskite films fabricated with (b-1) CB1, (b-2)

CB2, and (b-3) CB3, respectively (Scale bars: 1 µm).



Fig. 3. Schematics of possible incident light paths within PSCs made with CB1-PVK, CB2-PVK and CB3-PVK, respectively, and the cross-sectional SEM images of corresponding perovskite films (scale bars: 100 nm).

intermediate phase transformation, *in situ* temperature-dependent X-ray diffraction (XRD) spectra of CB2-induced film at different annealing temperatures were measured in a non-vacuum environment. Fig. 5a demonstrates the full-scan diffractograms obtained at different annealing temperatures from 25 °C (i.e., room temperature) to 130 °C. Clearly, the resultant intermediate phase is self-organized and highly crystalline in nature. The peak positions of CB2-UCF (25 °C: black line) are identical to those observed in MAI-PbI₂-DMSO single crystals: the typical peaks at 6.76° , 7.46° and 9.38° correspond to the (0 0 2), (0 2 1) and (0 2 2) peaks of MAI-PbI₂-DMSO, implying that MAI and DMSO molecules have successfully intercalated into the PbI₂ inter-layer [38].

When increasing the annealing temperature from 25 to 130 °C, the initial peaks gradually disappear while some new characteristic peaks centered around 14.01°, 19.81°, 23.48°, 24.39°, 28.25° and 31.77° are observed. The latter are attributed to tetragonal MAPbI₃ (1 1 0), (1 1 2), (2 1 1), (2 0 2), (2 2 0) and (3 1 0), respectively (marked with " \diamond " dots) [40]. Additionally, a clear preference for growth along the (1 1 0) orientation plane can be observed. The MAI-PbI₂-DMSO intermediate phase can be fully converted into a pure MAPbI₃ phase when the

annealing temperature is higher than 60 °C (green line), whereas both MAI-PbI₂-DMSO and MAPbI₃ phases coexist at 40–50 °C (i.e., 40 °C: red line; 50 °C: blue line). In other words, the MAI-PbI₂-DMSO intermediate phase undergoes sufficient intramolecular exchange between MAI and DMSO, i.e., DMSO is completely removed from UCF, and then entirely converted into the MAPbI₃ phase when the annealing temperature is higher than 60 °C. As a result, we define 60 °C as the critical point of the complete phase transition in this work.

In addition, the MAPbI₃ (1 1 0), (2 2 0) and (3 1 0) peaks exhibit obvious enhancements and small angular shifts as the annealing temperatures increase, indicating that the lattice constant gradually increases, which further proofs that lattice distortion and crystal expansion occur during the phase transition [41]. Therefore, we can obtain high-quality HRT-perovskite absorbers from the porous-structured CB2-UCF, as confirmed by SEM imaging.

Finally, a weak PbI₂ (0 0 1) peak centered around 12.67° is observed in the film by further increasing the annealing temperature to 130 °C (marked with " \ast " symbol) [42], mainly due to the decomposition of the perovskite at high temperatures (as depicted in Fig. 5b).



Fig. 4. (a) UV-vis absorption spectra of perovskite films treated with CB1, CB2 and CB3, respectively; (b) Tauc plots of CB1-PVK film, CB2-PVK film and CB3-PVK film, respectively.



Fig. 5. In situ temperature-dependent XRD spectra of CB2-induced film at different annealing temperatures. (a) The panorama curves from 5° to 45° , (b-e) selected ranges containing particular characteristics; \diamond and \approx represent peaks for MAPbI₃ phase and PbI₂ phase, respectively.

The vacuum environment during SEM measurements accelerates the transition from the MAI-PbI2-DMSO phase to the MAPbI3 phase, thus UCFs in Fig. 2a are actually the coexistence morphology of intermediate mixtures and trace perovskite. The XRD patterns of CB2-UCFs tested with and without the vacuum environment are shown in Fig. S1[†]. In contrast with the CB2-UCF in a non-vacuum environment, three diffraction peaks located at 14.01°, 28.25° and 31.77° are observed for the vacuum-treated CB2-UCF, which can be assigned to the MAPbI₃ (1 1 0), (2 2 0) and (3 1 0) peaks (marked with "\$" dots). Moreover, the diffraction peak of ITO-glass is commonly used as a datum of peak position (marked with " \triangle " dot), and the unlabeled diffraction peaks are consistent with the diffraction pattern of the MAI-PbI2-DMSO intermediate phase. Similarly, in situ temperature-dependent XRD spectra of CB2induced film under vacuum conditions further demonstrate that vacuum environment can greatly accelerate the formation and decomposition of the perovskite film (as shown in Fig. S2[†]). Different from

Fig. 5, the MAPbI₃ (1 1 0), (2 2 0) and (3 1 0) peaks increase initially and then decrease with increasing the annealing temperature (marked with " \diamond " dots), and reach the maximum value at 100 °C. In addition, a small amount of PbI₂ precipitates from the perovskite at 100 °C, while the MAPbI₃ phase completely decompose into PbI₂ phase at 130 °C [42]. This analysis indicates that films should be tested in a non-vacuum environment to ensure accuracy of results.

Fourier transform infrared (FTIR) spectroscopy was employed to further analyze the formation mechanism of the CB-induced HRT-perovskite absorber. MAI-PbI₂-DMSO and corresponding MAPbI₃ spectra are shown in Fig. S3† (Supporting Information). The S=O (ν (S=O)) stretching bond is located at 1045 cm⁻¹ in DMSO solvent [40], but clearly shifts to a lower wavenumber of 1015 cm⁻¹ in the as-fabricated MAI-PbI₂-DMSO film (black line) [43]. According to harmonic motion for a diatomic model [44], frequency of vibration is proportional to the square root of the force constant. Hence, the decreased S=O stretching



Fig. 6. XRD patterns of (a) UCFs fabricated with different CB dipping amounts (CB1, CB2 and CB3, respectively), and (b) the corresponding perovskite films.

frequency implies a decrease in bond strength between S and O as a consequence of the intermediate phase formation, i.e., the formation of the MAI-PbI₂-DMSO phase is attributed to the interaction of Lewis base DMSO and/or iodine (I⁻) with Lewis acid PbI₂ [45]. In addition, C-H (ν (C–H)) stretching peaks (in the range 2800–2950 cm⁻¹) in the asfabricated MAI-PbI₂-DMSO film stem from the -CH₃⁺ group in the DMSO molecule [40]. Clearly, for the MAPbI₃ film, the obvious attenuation of the stretching peaks of ν (S=O) and ν (C-H) mentioned above can be regarded as an important indicator for the removal of DMSO from the MAI-PbI₂-DMSO film, implying the complete formation of the MAPbI₃ phase [2,14]. Moreover, the N–H (δ (N–H)) stretching and bending vibration emerges simultaneously (in the range $3200-3450 \text{ cm}^{-1}$ and at 1634 cm⁻¹, respectively), indicating the hydrogen-bonding interaction increases with the formation of the MAPbI₃ phase. These FTIR, XRD and SEM results together reveal the formation mechanism of the CB-induced HRT-perovskite absorber. The corresponding chemical reaction process is schematically displayed in Fig. S4†.

To qualitatively evaluate the influence of CB dipping amounts on the crystallization kinetics of MAPbI₃, the XRD patterns of UCFs and corresponding perovskite films are illustrated in Fig. 6a and b, respectively. The diffraction peaks of all UCFs are consistent with those of the pure MAI-PbI₂-DMSO intermediate phase, and no new characteristic peaks are observed, indicating that the increase of CB dipping amounts cannot lead to lattice reconstruction and/or the formation of new components, as shown in Fig. 6a. In addition, the diffraction peaks of MAI-PbI₂-DMSO are almost unchanged, implying that different CB dipping amounts have little effect on the crystallization kinetics of intermediate complexes. Therefore, the morphological differences of UCFs are mainly attributed to the role of residual solvents in films under different volumes of CB treatments.

Subsequently, Fig. 6b indicates that the peak intensity of CB2-PVK film is higher than that of CB1-PVK and CB3-PVK films, especially the MAPbI₃ (1 1 0) plane, which further shows that the morphology of CB-induced UCFs plays a predominant role in the lattice orientation selection and crystallinity optimization in the perovskite formation process. Furthermore, the full width at half maximum (FWHM) of the CB2-PVK (1 1 0) plane is narrower than the other two samples, in the order

CB2-PVK ($\sim 0.17^{\circ}$) < CB3-PVK ($\sim 0.19^{\circ}$) < CB1-PVK (0.23°), also indicating the improvement of crystallinity. Therefore, as analyzed from the above SEM, UV and XRD results, we believe that the CB dipping amount is the key to regulating the structural characteristics of the perovskite, and an optimum CB volume is essential for constructing porous UCFs and forming high-quality HRT-perovskite absorbers.

Steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) techniques are generally considered the most effective methods to characterize the carrier dynamics of photoactive materials. The emission peak located at ~773 nm is related to the direct band-gap emission of MAPbI₃ film, and the relative PL peak intensity can be used to estimate the electron–hole pair recombination behavior. The steady-state PL spectrum of ITO/SnO₂/CB2-PVK substrate shows a lower quenching intensity than the other two samples, implying a better charge extraction/collection efficiency (the inset in Fig. 7a).

The corresponding TRPL decays are presented in Fig. 7a. The excitons and/or carrier lifetimes of samples treated with different CB dipping amounts are obtained by fitting relaxation curves with double exponential decay function, as shown below:

$$f(t) = A_0 + A_1 \exp(-t/t_1) + A_2 \exp(-t/t_2),$$
(2)

where A_0 is a constant for the baseline offset. τ_1 and τ_2 are utilized to present the efficiency of charge separation and injection, i.e., τ_1 is the fast decay time responsible for interface recombination and τ_2 is the slow decay time responsible for bulk recombination. A_1 and A_2 are the corresponding decay amplitudes [46]. The kinetic parameters of the TRPL data are displayed in Table S1†. The PL decays of CB1-PVK, CB2-PVK and CB3-PVK sandwiched between SnO₂ and Spiro-OMeTAD layers exhibit two lifetime constants of $\tau_1 = 6.58$ ns and $\tau_2 = 97.89$ ns, $\tau_1 = 5.26$ ns and $\tau_2 = 80.17$ ns, $\tau_1 = 7.25$ ns and $\tau_2 = 117.61$ ns, respectively. Clearly, the carrier lifetimes of ITO/SnO₂/CB2-PVK/Spiro-OMeTAD substrate are shortest (both on the interface and in the bulk), indicating an improved carrier separation and collection from the HRTperovskite configuration, which is consistent with the discussions mentioned above.

To quantitatively evaluate the defect density and charge mobility of perovskite films, we fabricated the devices with ITO/CB-induced PVK/ Ag architecture, and described the space-charge-limited current (SCLC)

Fig. 7. (a) TRPL plots and fitting curves of ITO/ SnO₂/CB-induced MAPbI₃/Spiro-OMeTAD substrates fabricated with different CB dipping amounts, (b) Nyquist plots, (c) *J*–V curves and (d) corresponding EQE spectra of PSCs fabricated with CB1, CB2 and CB3, respectively. The inset of (a) shows the steadystate PL spectra of ITO/SnO₂/CB-induced MAPbI₃ (i.e., CB1-PVK, CB2-PVK and CB3-PVK) substrates. The inset of (b) depicts the equivalent circuit model of fitted EIS. The inset of (c) depicts the steady-state photocurrent of the corresponding devices. The inset of (d) shows the cross-section SEM image of CB2-PSC.



based on different CB treatments. The dark current-voltage (*J-V*) curves are shown in Fig. S5†. The trap filling voltage determines the trap state density, and the defect density ($N_{defects}$) affects charge mobility, i.e., a decrease of $N_{defects}$ increases charge mobility [5,47]. The equation is as follows: $N_{defects} = (2\varepsilon_0\varepsilon_r V_{TFL})/qL^2$, where ε_0 is the vacuum permittivity (8.85 × 10⁻¹² F m⁻¹), ε_r is the relative dielectric constant (MAPbI₃ \approx 34), V_{TFL} represents the trap-filling limited voltage, q is the elemental charge, and L is the thickness of the obtained perovskite films [48,49]. Obviously, the V_{TFL} values shown in Fig. S5a–c† are 0.178, 0.101 and 0.216 V for the CB1, CB2, and CB3 samples, respectively. Therefore, the corresponding $N_{defects}$ were estimated to be 1.67 × 10¹⁵, 9.21 × 10¹⁴ and 1.97 × 10¹⁵ cm⁻³, respectively. The low defect density of CB2-PVK can effectively improve charge mobility, thus inhibiting the charge accumulation at the surface/interface of perovskite and contributing to improving device performance.

To gain further insight into the interfacial charge transport and recombination process, electrochemical impedance spectroscopy (EIS) of the as-fabricated devices was measured at a voltage bias of 0.8 V in the absence of light [46]. The corresponding Nyquist spectra are fitted with an electrical equivalent circuit model shown in Fig. 7b, where $R_{\rm S}$ represents the series resistance due to ohmic or electrical contacts and associated with a high-frequency spectrum, Ctr represents the geometrical capacitance associated with a high-frequency spectrum, $C_{\rm rec}$ represents the capacitance due to interface charge or ion accumulations and associated with a low-frequency spectrum, and R_{tr} and R_{rec} represent resistance (i.e., charge transport and recombination resistance, respectively) associated with high- and low-frequency spectra and related to recombination processes occurring at the interface of PSCs [50]. Compared with the other two devices, the device based on HRTperovskite absorber (i.e., CB2-PVK) exhibits the smallest high-frequency arc and the largest low-frequency arc, which indicates that the corresponding perovskite upper and lower hetero-interfaces have excellent charge extraction/collection efficiency and the smallest carrier recombination loss, thus helping to improve J_{SC} , FF and PCE of PSC.

The *J*–*V* characteristics of PSCs treated with different CB dipping amounts are presented in Fig. 7c, and the detailed photovoltaic parameters are summarized in Table 2. The experimental details of the PSCs fabrication can be found in the Section 2. We named these as-prepared devices as CB1-PSC, CB2-PSC and CB3-PSC in the following discussions, respectively. The *J*_{SC}, *FF* and PCE increase initially and then decrease with increasing CB amounts, and the CB2-PSC exhibits the highest photovoltaic performance under AM 1.5G illumination conditions (100 mA cm⁻²), which is consistent with the above results. In addition, the relatively poor electrical properties of the CB1-PSC and CB3-PSC should be attributed to charge recombination around the abundant grain boundaries and defects. Ultimately, the device fabricated using CB2-induced HRT-perovskite absorber shows the best performance: *J*_{SC} of 23.02 mA cm⁻², *V*_{OC} of 1.08 V, *FF* of 78.84%, and PCE of 19.60%, respectively.

The steady-state photocurrent densities measured at constant biases of 0.91 V, 0.91 V and 0.89 V near the maximum power point (V_{mp}) for the corresponding devices (CB1-PSC, CB2-PSC and CB3-PSC, respectively) are shown in the inset of Fig. 7c. Consistent with the results of J-V, the J_{SC} of CB2-PSC is higher than the other two devices, and its value remains nearly constant by light-soaking under 1 Sun for 200 s. This tendency can also be verified by the external quantum efficiency (EQE) values, and the corresponding EQE spectra of the devices are shown in Fig. 7d. A more stable and stronger spectral response in the range below 750 nm is observed for CB2-PSC compared with the other two devices, mainly due to the high-quality HRT-perovskite absorber induced by CB2 has i) excellent carrier transport efficiency from perovskite to adjacent contacts and ii) superior light harvesting capabilities over the same spectral region. A typical cross-section SEM image of corresponding CB2-PSC is also presented in the inset of Fig. 7d.

Moreover, reproducibility is critical for the practical use of PSCs, and the reliability of the device performance is verified through fabrication of 20 individual devices. For each fabrication condition, the efficiency statistical histograms of three groups of devices are shown in Fig. S6[†]. The average efficiency of CB2-PSCs (~19.00%) is significantly higher than that of CB1-PSCs (~17.11%) and CB3-PSCs (~15.95%), and the standard deviation of efficiency for CB2-PSCs (~0.86) is significantly lower than the other two devices, i.e., CB1-PSCs (~1.39) and CB3-PSCs (~0.96). In consideration of the same ETLs and HTLs used for the above devices, this efficiency enhancement and relatively narrow efficiency distribution should be attributed to the optimized CB2-induced HRT-perovskite absorbers being able to maintain good film uniformity, high light-capture ability and excellent charge separation/ collection efficiency in 20 different individual devices. Therefore, our results indicate that high-performance PSCs can be repeatedly fabricated by using a simple CB2 treatment. For the champion device we obtained an efficiency of 20.03%, a J_{SC} of 22.98 mA cm⁻², a FF of 77.53%, and a $V_{\rm OC}$ of 1.12 V, and there is a very small hysteresis for the device. The corresponding reverse and forward J-V curves and EQE spectrum are shown in Fig. 8a and b, respectively. There is a broad EQE plateau above 85% over the spectral range from ~400 to 750 nm because of efficient light harvesting within the CB2-induced HRT-perovskite absorber. The integrated current density from the EQE is 22.19 mA cm⁻², which is almost in agreement with the J_{SC} value from J-V characterization.

Furthermore, the J_{SC} , V_{OC} , *FF* and PCE statistics of 20 individual devices employing the same optimized conditions are summarized in Fig. S7a†. The V_{OC} values of all devices exhibit slight changes, but the J_{SC} and *FF* values exhibit obvious fluctuation, which might result from the inherent difference in the thickness of Spiro-OMeTAD HTLs deposited by spin-coating. Consequently, an average PCE of 19.00% with an average J_{SC} of 22.56 mA cm⁻², an average V_{OC} of 1.08 V and an average *FF* of 77.31% can be achieved under standard AM 1.5G conditions.

As shown in Fig. S7b†, we also evaluate the stability of the CB2induced device. The unencapsulated device with CB2 treatment only decreases by ~0.33% compared with its initial PCE after ~500 h, indicating a relatively good stability. The device was stored in a dry box (relative humidity < 20%) at room temperature (~25 °C) to measure its reverse *J*–*V* curves regularly. Not surprisingly, the *FF* and PCE increased significantly in the first 100 h after the oxidation of Spiro-OMeTAD HTL, and decreased slightly over time. This may be due to the gradual degradation of Spiro-OMeTAD and perovskite caused by the long-term exposure of unencapsulated device to the atmosphere. As a result, we achieved a stable PCE of approximately 19.21%, with the V_{oC} is higher than 1.12 V, the average photo-current of 22.90 mA cm⁻², and average *FF* of 74.73%.

4. Conclusion

In summary, we improved the performance of planar heterojunction PSC by using a HRT-MAPbI₃ absorber realized with a convenient CB anti-solvent-assisted spin-coating method. In particular, we found that optimal CB volume promoted the construction of a loose and porous MAI-PbI₂-DMSO intermediate structure, revealing the function of CB in the growth of the HRT-perovskite absorber. Moreover, the porous nature of the intermediate film has been shown to be essential for the realization of the HRT-perovskite absorber, as it provides sufficient space for the lattice reconstruction and structure expansion during

Table 2	
Photovoltaic parameters derived f	from the corresponding J-V curves.

			-	
Devices	$J_{\rm SC}~({ m mA~cm^{-2}})$	$V_{\rm OC}$ (V)	FF (%)	<i>Eff.</i> (%)
CB1-PSC	20.82	1.08	76.69	17.34
CB2-PSC	23.02	1.08	78.84	19.60
CB3-PSC	21.64	1.02	74.94	16.54



Fig. 8. (a) The reverse and forward J-V curves of the champion device measured under standard AM 1.5G illumination (100 mA cm⁻²). (b) Corresponding EQE spectrum and integrated J_{SC} .

crystal growth. Compared with traditional textured perovskite absorbers, the HRT-MAPbI₃ absorber with large grain size, appropriate surface roughness, longitudinally ordered grain boundary distribution and large specific surface area exhibited excellent light-harvesting capability and photo-generated charge separation/collection efficiency. As a result, the practical planar heterojunction device (~400 nm-thick HRT-perovskite absorber) efficiency was enhanced to 20.03% with a J_{SC} of 22.98 mA cm $^{-2}$, a FF of 77.53% and a V_{OC} of 1.12 V. In addition, an average PCE of 19.00% was achieved in 20 individual devices fabricated with the same optimized procedure, implying good reproducibility. Additionally, all processes were conducted at a relatively low temperature (≤150 °C), which is convenient for a wide range of applications, such as flexible- and tandem- solar cells on thermal-sensitive substrates. The present work provides new concepts for the design of new PVK absorbers and lays a foundation for further realization of higher PCE in PSCs.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors gratefully acknowledge the support from National Natural Science Foundation of China (Grant Nos. 61904066, 61775081, 11904127, 61705079 and 51902126), Program for the development of Science and Technology of Jilin province (Item No. 20180519016JH, 20180520182JH, 20190701021GH and 20190103039JH), and the Thirteenth Five-Year Program for Science and Technology of Education Department of Jilin Province (Item No. JJKH20190998KJ and JJKH20191019KJ).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2020.124091.

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