

Fast and Controllable Electric-Field-Assisted Reactive Deposited Stable and Annealing-Free Perovskite toward Applicable High-Performance Solar Cells

Feng Zhou, Hong Liu,* Xinwei Wang, and Wenzhong Shen*

Recently, organic–inorganic hybrid perovskite materials have drawn great attention for their outstanding performance in high-efficiency solar cells. Successful synthesis has been realized either in solution-based chemical deposition or vapor deposition. However, conflicts have never ceased among quality control, growth rate, process complexity, and instrument requirement, which have limited their development toward real applications. In this work, the first electrochemical fabrication of perovskite toward high-efficiency and scalable perovskite solar cells (PSCs) is established. The morphology and crystallization of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ film can be effectively controlled by simply modulating a few physical parameters. A detailed study on its optoelectronic properties reveals significantly improved film quality and interfacial conditions. Aided by this, the total process does not require standard annealing, which greatly reduces the total growth time from hours to minutes. Up to now, an efficiency of 15.65% has been achieved in planar PSCs under 1 sun AM 1.5 condition, with small hysteresis and efficiency loss under longtime exposure to air. Moreover, high efficiency (10.45%) can be easily attained for large cells (2 cm^2). This result will hopefully facilitate research for applicable high-efficiency PSCs and other multicomponent materials as well.

1. Introduction

In the past few years, organic–inorganic hybrid perovskite materials have attracted great attention owing to their remarkable and unique photovoltaic properties such as high electron and hole mobility,^[1,2] tunable optical bandgaps,^[3] and strong absorption of light.^[4] Starting from the pioneer work with 3.8% efficiency in sensitized solar cells by Miyasaka and co-workers,^[5] vast development has been accomplished since the works with maiden power conversion efficiency (PCE) of 15.0% in mesoporous structure perovskite solar cell (PSC) by Grätzel and co-workers and 15.4% in planar PSC by Snaith and

co-workers^[6,7] with solid-state electrolyte. Despite variations, all current methods can be generally summed up as two types: liquid-phase sequential chemical deposition (in which one- and two-step spin-coating are involved) and gaseous-phase reactive deposition. As the earliest investigated reaction type, the liquid-phase chemical deposition (including one and two-step spin-coating reaction) has been frequently used due to low equipment requirement and easy-to-operate processes. It has achieved many milestones in the research toward efficient, stable, and reproducible perovskite optoelectronic devices.^[8–14] As another major method, gaseous-phase deposition has also undergone significant achievements, especially on planar-type perovskite cells.^[6,15] Further achievements have been attained by developing blade-coating,^[16] solvent engineering,^[17–19] new types of compound,^[15,20,21] and modifying the carrier transport layers/interfaces^[22–24] based on

studies crossing various scientific fields. Until now, a stable efficiency of up to 21.1% was reported in $\text{Cs}_x(\text{MA}_{0.17}\text{FA}_{0.83})_{1-x}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ system with doped TiO_2 substrate by Grätzel and co-workers^[25] (a higher record of 22.1% has been announced by Solliance).^[26] Furthermore, recent focus of the perovskite has been expanded to hysteresis,^[27–29] stability,^[30,31] and optoelectronic mechanism^[32,33] toward feasibility of the perovskite cells. Nevertheless, these developments have still more or less been bound to the two types of growth systems that require either complex fabrication steps or instrumental conditions such as vacuum circumstance. Moreover, most of these methods have included thermal annealing at 70–150 °C for hours. The more steps or treatments or chemicals be added, the more complexity will be induced and the reproducibility will also be influenced. To resolve this, the formation mechanism of perovskite itself could also be important for research in this field and for some essential change from another angle of view, with which only few studies have been focused on.

From this concern, introduction of an external physical field such as electrical field would hopefully significantly influence the process due to the existence of ionic species (CH_3NH_3^+ or MA^+ , I^- , Pb^{2+}) in those systems. Up to now, the only related works have been made by introduction of some electrochemical means as one preliminary step in the normal solution-based fabrications of perovskite, forming Pb oxides prior to reaction

F. Zhou, Dr. H. Liu, X. W. Wang, Prof. W. Z. Shen
Institute of Solar Energy
Key Laboratory of Artificial Structures and
Quantum Control (Ministry of Education)
Department of Physics and Astronomy
Shanghai Jiao Tong University
Shanghai 200240, P. R. China
E-mail: liuhong@sjtu.edu.cn; wzshen@sjtu.edu.cn



Prof. W. Z. Shen
Collaborative Innovation Center of Advanced Microstructures
Nanjing 210093, P. R. China

DOI: 10.1002/adfm.201606156

with MA species.^[34–36] That is to say, they were basically still a sort of spin-coating chemical fabrication and it still remained unknown whether a complete electrochemical growth of perovskite is possible since it has more than three components, whether its performance is comparable to the conventionally fabricated ones, and whether any significant difference can be brought into the material and the method itself. In our previous research on electrochemical fabrication of PbS and CdS nanostructures, both cationic and anionic components can be effectively formed by suitable control of electric signal of bias applied on the substrate, indicating a possible route for multiple component materials, too.^[37,38] Furthermore, it has also been found that electric field can significantly influence the crystallization during electrochemical process of materials in liquid phase,^[39,40] which implies another probable support from the introduction of electric field.

In this work, we report a novel controllable and efficient electrochemical synthesis of hybrid perovskite materials toward photovoltaic devices. High-quality annealing-free perovskite of several hundred nanometers thickness can be grown within a few minutes with modulation of only a few physical parameters. More detailed study of the mechanisms has indicated the main enrolment of ionic species Pb^{2+} , MA^+ , and I^- in the formation of perovskite via thermal diffusion and directional drifting under electric field. The whole process can be controlled simply by a few electric parameters such as frequency, amplitude, and waveform of the alternating current (AC) voltage applied during the reaction. The as-fabricated perovskite has shown an interesting anti-Stokes shift of the photoluminescence (PL) characteristics and quite good carrier transport ability when simply tuning the controlling voltage according to systematic absorption, PL, time-resolved photoluminescence (TRPL), and electrochemical impedance spectroscopy (EIS) measurement. Evidence has also shown that certain current annealing effect has assisted in the material formation so that a compact perovskite film with uniform crystalline grains has been formed and thus no conventional thermal annealing was needed. The as-prepared solar cell has shown an efficiency up to 15.65% ($V_{\text{OC}} = 1.098 \text{ V}$, $J_{\text{SC}} = 20.99 \text{ mA cm}^{-2}$, and $\text{FF} = 67.91\%$) with low hysteresis and high stability with degradation of efficiency less than 0.7% after initial 24 d. Eventually, quite good scalability has also been found when a 10.45% efficiency was obtained using large effective area (2 cm^2), which is still expandable with further improvement on electrode size and other conditions.

This result would probably be helpful for the future development of perovskite studies toward stable and applicable devices, as well as for better understanding on the material formation mechanisms.

2. Results and Discussion

2.1. General Concept and Preliminary Experiments

In most previous formation systems of perovskite, the precursors of Pb have appeared in the form of ionic compounds and the precursors of MA in the form of its halogen compounds. Hence, a possible electrochemical experiment can consist of a few major processes, namely, the dispersion and adsorption of Pb precursor, ionization of Pb and MA precursors, and reaction of ionized species. Moreover, the ionization of halogen ions can be easily achieved in different solutions and thus can be separately considered from that of Pb ions. Hence, for better controllability, we have divided the total method into two steps, as shown in **Figure 1**. In step 1, a Pb thin film was electrodeposited onto a fluorine-doped tin oxide (FTO) glass substrate coated with a thin compact TiO_2 (c-TiO_2) in a mixed isopropanol solution of PbI_2 and NaI (which provide I^- ions to assist the dissolution of PbI_2 in the isopropanol, $\text{PbI}_2 + x\text{I}^- \rightarrow \text{PbI}_{2+x}^{x-}$, $x = 1, 2$).^[41] In step 2, the sample was transferred into isopropanol solution of methylammonium iodide (MAI) and perovskite was formed under manipulated voltage applied on the pool. Finally, the perovskite film was dried by N_2 flow for PSC fabrication. The real pictures of samples can also be seen from **Figure 1**, which has indicated formation of perovskite by a conversion from an initially semi-transparent surface to a finally dark surface.

Initially, all electrochemical conditions were set potentiostatic, which means a constant bias voltage at -2.5 V in step 1 and then a subsequent constant bias voltage at $+2.5 \text{ V}$ in step 2. The amplitude of bias was chosen to adequately assist the reaction and avoid inhomogeneity of the product at higher voltage. As shown in **Figure 2a–d**, certain deposits covered the substrate surface after the first step and then were replaced by certain rectangular-shaped particles after the second step. The as-formed materials have been integrated into a typical planar PSC with its morphology shown in **Figure 2e**. Further structural and elemental analysis in **Figure 2f** and **Table 1** has proved that the products after step 1 and 2 are corresponding to Pb

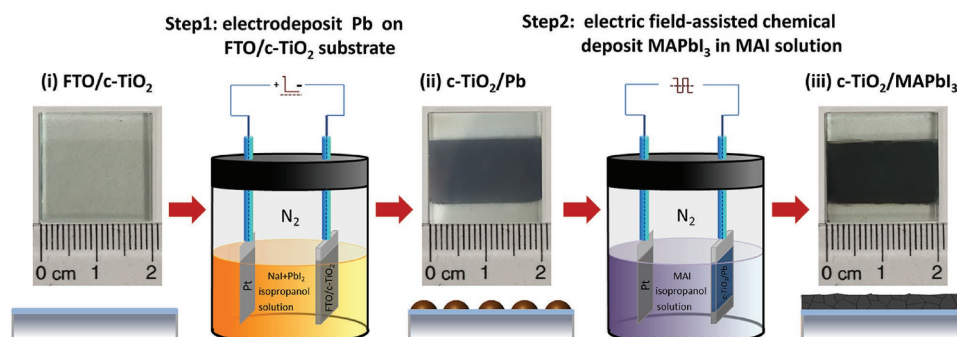


Figure 1. Schematic illustration of two-step electrodeposition of MAPbI_3 . Pictures of the sample before step 1 of the reaction, between step 1 and 2, and after step 2 are marked by (i), (ii), and (iii), respectively. Corresponding surface morphology is displayed below the picture.

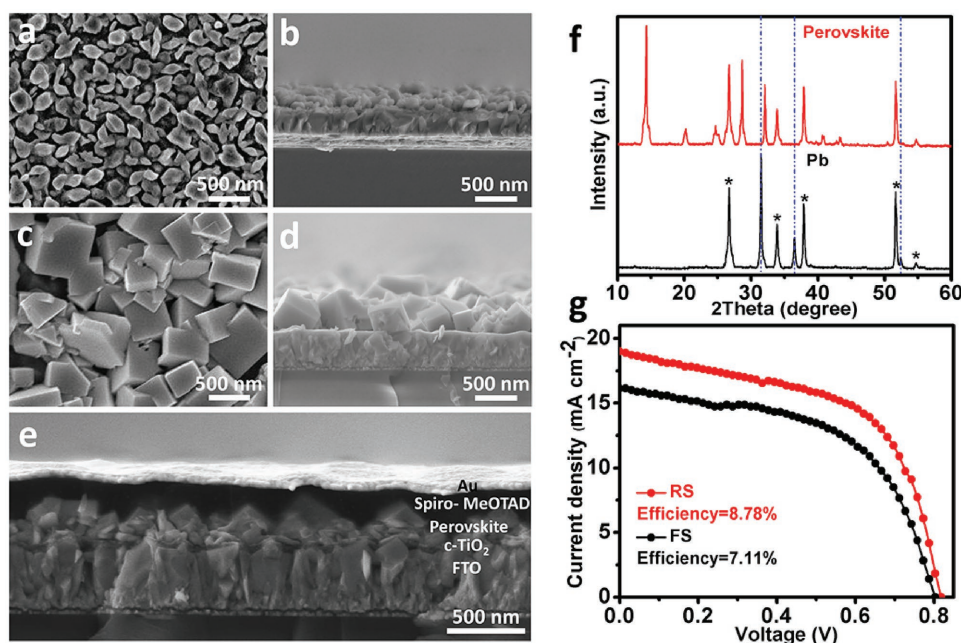


Figure 2. Characterization of MAPbI₃ film prepared under potentiostatic condition. SEM images of the sample after step 1: a) top and b) cross-sectional view at -2.5 V, $t = 5$ min. SEM images of the sample after step 2: c) top and d) cross-sectional view at $+2.5$ V, $t = 5$ min. e) SEM cross-sectional view of as-fabricated solar cell. f) XRD pattern of samples after step 1 and 2; the symbols “*” and dashed lines represent the peaks of FTO/c-TiO₂ substrate and Pb film, respectively. g) J - V characteristics of the as-fabricated perovskite cells.

deposits and perovskite grains, respectively (details of energy dispersive spectrometer (EDS) measurement can be found in Figure S1, Supporting Information). The perovskite thickness was about 480 nm. After integration of the as-fabricated perovskite film into the solar cell, a PCE of 8.78% (reverse sweeping) with a forward sweeping PCE of 7.11% (Figure 2g) was eventually yielded, indicating an announcing initial efficiency.

Nevertheless, it was still a significantly lower value compared to typical efficiencies of the perovskite cells.^[6,7] As shown in Figure 2, this might be at least partly attributed to the morphology of the as-formed perovskite film that contained large grains with significant size variation and large spacing between the grains, which can strongly influence the carrier transportation at the interfaces and the optoelectronic properties in the light-absorption layer in the fabricated solar cells.^[11,42,43]

2.2. Manipulate Step 1: Pb Deposition

To resolve this, more details of the two main steps should be studied. First of all, the Pb particles in step 1 appear to be the basis of the perovskite growth in step 2. Therefore, the nucleation and growth of Pb particles would be the first issue in controlling the perovskite formation. Assuming that the growth rate of Pb is the same with different initial nuclei density in

the beginning of step 1 under identical situation, the final coverage of Pb would be directly proportional to the initial nuclei density. Hence, higher density of Pb nuclei in step 1 would be helpful in the formation of more compact perovskite film and in the meantime accelerate the increase of the perovskite coverage. Besides, an adequate limit of the density and size of Pb nuclei will also be necessary if taking into account the volume expansion during the transformation from Pb to perovskite. Hence, for effective control of nuclei growth, high amplitude of bias was chosen as the key factor for development of higher-density crystal nuclei, as commonly known in electrodeposition systems.^[44] Therefore, we applied a high voltage pulse at the beginning of step 1 with different amplitude from -2.5 to -25 V, followed by a constant bias at -2.5 V with different deposition time. The pulse length was set very short (1 s) to avoid strong nonuniformity of the products under strongly enhanced distortion of surface field at high bias amplitude for a long period. It has been found that -20 V pulse amplitude (1 s) is the optimized condition for perovskite and PSC fabrication with highest nuclei density of Pb and island size (detailed measurement method and data can be found in Figures S2–S4, Supporting Information). As can be observed in Figure 3, the island density and size of Pb was much higher than the one in Figure 2 and the resulted perovskite has more uniform and smaller grain size, which can induce less vacancy of as-formed

Table 1. EDS characterization of the sample content in corresponding steps.

Elements		Ti	O	C	N	Pb	I
Atomic percentage [%]	Step 1	36.04	13.51	0	0	50.45	0
	Step 2	0	0	27.72	8.22	16.01	48.05

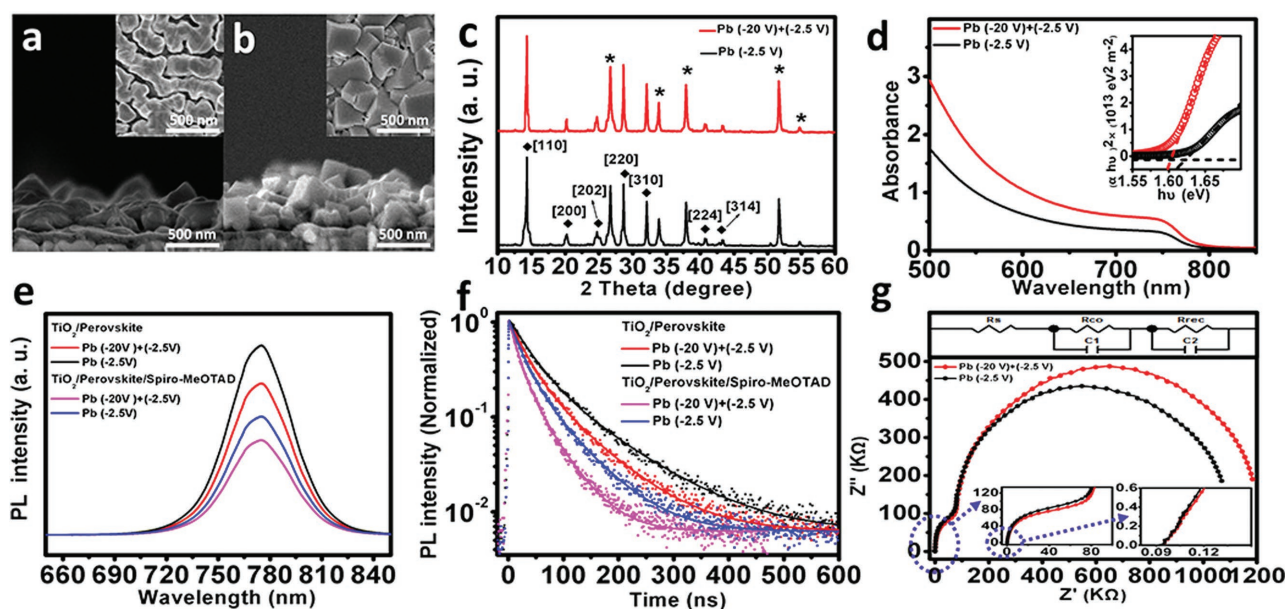


Figure 3. Effect of pulse modulation in Pb deposition stage. a,b) SEM images of Pb nuclei formed with pulse modulation (-20 V, 1 s) and corresponding perovskite, respectively. c) XRD of samples without and with pulse modulation; the symbols “*” represent the peaks of FTO/c-TiO₂ substrate. d) Absorption of samples without and with pulse modulation. e,f) PL and TRPL of samples without/with pulse modulation and without/with spiro-MeOTAD above perovskite, respectively. g) EIS measurements of samples without/with pulse modulation, together with equivalent circuit on top.

perovskite film. Following with the fabrication of corresponding PSC has yielded a best PCE of 11.5% (Table S1, Supporting Information), significantly higher than the result in Figure 2. We have further characterized the samples before and after modulation in the Pb formation stage to investigate the origin.

Compared to the condition without modulation (Figure 2), the X-ray diffraction (XRD) of the perovskite with pulse modulation in the Pb stage has shown narrower peak width, especially the ones in the [110] and [202] direction. It indicates that the pulse applied in the Pb formation stage has significantly induced more organized crystallization in the later fabricated perovskite. The as-fabricated samples were then characterized by combined methods to investigate their optoelectronic property and its relationship with experimental conditions. Since perovskite can transport electrons and holes, samples were fabricated without and with 2,2',7,7'-tetrakis(*N,N*-di-4-methoxyphenylamino)-9,9'-spirobifluorene (spiro-MeOTAD) above the perovskite layer to better understand their involvement (configuration of samples can be found in Figure S5, Supporting Information). As shown in absorption spectra in Figure 3d, the absorption edge is located at about 764 and 778 nm for the samples before and after pulse modulation in Pb formation, respectively. In the meantime, the PL peaks of all samples (with/without spiro-MeOTAD, before/after Pb modulation) are located at about 775 nm (Figure 3e). This has indicated a significant transition from Stokes to anti-Stokes shift in the electrochemical fabricated perovskite after the pulse modulation in step 1. The Stokes shift is normally due to vibrational relaxation in the perovskite in the preliminary experiment without any optimization, which has been seen in XRD with less organized structure than the sample with pulse modulation. The anti-Stokes shift has been well known in yttrium oxysulfide doped with gadolinium oxysulfide and is in this work

possibly contributed to dissipation of thermal photons in lattices of perovskite grains according to previous works.^[45]

Moreover, the PL spectra of the perovskite samples with spiro-MeOTAD before and after Pb modulation have both shown great intensity reduction compared to the one without it. It indicates a strong involvement of holes in the general carrier transport of the as-fabricated perovskites.^[46] In the meantime, as shown in Figure 3f, the TRPL of the sample with spiro-MeOTAD hole transport layer (HTL) has also shown significantly faster PL decays than the one without it (details can be found in Table S2, Supporting Information) with lifetime decreasing from 104.90 to 80.04 ns without HTL and from 64.90 to 46.53 ns with HTL, respectively. Considering the influence of the spiro-MeOTAD on the diffusion of holes, the lower PL peak and faster PL decays with HTL compared to the one without it can be attributed to lower carrier density due to enhanced hole transport with the HTL. Second, if we compare the samples before and after Pb modulation under the same condition, it can be seen that in both cases (with/without HTL) there was significant reduction in PL peak and faster PL decays after modulation in the Pb formation. Taking into account the narrower peaks in the XRD after Pb modulation, it is likely that the application of electric pulse in Pb formation has resulted in the sample's lower recombination and better transport ability of carriers.

To better study the carrier recombination and transport process, the samples have been further investigated by EIS. As shown in Figure 3g, the Nyquist plot is composed of two arcs: a small arc at high frequency and a large one at low frequency. The equivalent circuit is shown in the upper part of Figure 3g. According to discussion in previous research works,^[47,48] the intercept at the Z' axis, the small and the large arcs are related to the series resistance R_s (accounting the resistance of all

layers including the electrode), the contact resistance R_{co} , and the resistance of recombination R_{rec} , respectively. As indicated by Figure 3g, R_s has no significant change before and after the modulation in Pb deposition. However, the R_{co} has shown significantly lower contact resistance R_{co} after modulation, which can be related to improved interface of ETL/perovskite and perovskite/HTL with fewer defects. Moreover, the large arc at low frequency has shown significantly higher resistance of recombination in the sample after Pb modulation, which indicates that fewer recombination centers existed in the sample after the pulse modulation in the Pb formation stage. Considering the XRD result, less recombination is seemingly due to better organization of crystalline structure in the grains toward more uniform lattice constant.

2.3. Manipulate Step 2: Perovskite Formation

Starting from the manipulation of Pb formation, two important issues still remained toward further improvement for the perovskite formation in step 2: (1) What are the key physical and chemical processes? and (2) Are they controllable? For the first question, under positive bias, a most probable process is that I^- anions were drifted by the electric field with direction pointing from the substrate to the electrolyte and MA^+ cations diffused toward the Pb surface, and then the two precursors react with the Pb to form perovskite. However, it is unknown how the Pb has taken part in the perovskite formation. To investigate this, an experiment was performed in the second step with and without electric bias. As a result, almost no perovskite was formed without the applied positive bias on the substrate (details can be found in Figure S6, Supporting Information). This strongly suggested that the main reactive precursor for Pb in $CH_3NH_3PbI_3$ ($MAPbI_3$) formation is more likely the ionic Pb^{2+} generated by reoxidation of the Pb particles by the positive bias instead of atomic Pb. Accordingly, the main reaction species contains both cations (Pb^{2+} , MA^+) and anion (I^-). Therefore, it is possible to attain effective control of the perovskite formation simply by electrochemical parameters such as time, amplitude, and waveform of applied electric signals. However, the electric field generated by constant positive bias would continuously induce repulsive force on the cations and thus reduce their concentration during the reaction so as to decelerate the final formation of perovskite. Specifically, since the generation of Pb^{2+} is also proportional to the positive voltage, the repulsing effect cannot be simply diminished by reduction of positive bias. Hence, an alternative bias condition has been introduced in this multicomponent (Pb^{2+} , MA^+ , I^-) system with compensation of the repulsive effect, which was to some degree previously investigated in two-component systems.

To carry out this investigation, an asymmetric square-wave pulse voltage ($f = 5$ Hz) was introduced, with the amplitude of its first half-wave fixed at +2.5 V and the second half tuned from -0.5 to -2.5 V (details can be inferred from Figure S7, Supporting Information), while the growth time was kept constant at 5 min. The lower limit was set to -2.5 V to avoid possible dissolution of perovskite. As demonstrated in Figure 4, the perovskite thickness monotonously increased from 320 to 370 nm, while the grain size decreased with increasing amplitude of the

second half-wave of the bias (Figure 4a–f; the point of +2.5 V in Figure 4f is corresponding to the previous potentiostatic condition. Size distribution can be found in Figure S8, Supporting Information). Possibly, more negative bias in the second half-wave has provided stronger electric force that drives the Pb^{2+} ions toward the working electrode and resulted in more enrichment of Pb^{2+} ions in a smaller distance above the substrate. This could have induced a higher number of reaction sites on the surface and thus more perovskite grains with smaller sizes. What's more, the perovskite film has become apparently more flat and compact under more negative half-wave amplitude. Consequently, the representative $J-V$ characteristics and corresponding photovoltaic parameters of as-fabricated PSCs (Figure 4g,h) have shown that the main parameters such as PCE, V_{OC} , and FF have been significantly improved with smoother and more compact perovskite film under the modified electric field.^[49,50] In general, all results with different AC bias condition have shown higher performance than the case in potentiostatic condition (can be referred from Figure S4, Supporting Information). Eventually, the best power conversion efficiency of up to 15.5% has been achieved using the PSCs fabricated with the perovskite films prepared at -2.5 V (second half-wave).

To investigate the influence of experimental conditions in step 2 on their structural and optoelectronic properties, the as-fabricated samples were further investigated as in the previous section. Unlike the situation in previous experiments on Pb modulation, no significant difference was found in the XRD of samples under different conditions. However, in the optoelectronic investigation that followed up, significant change has been found in samples under different conditions. As shown in Figures 4 and 5, the absorption edge continuously shifted to the lower energy side (corresponding to a wavelength increasing from about 778 to 799 nm) when the amplitude of the second half-wave of the applied voltage became more and more negative, while the PL peak remained at around 775 nm. It has shown a continuously enhanced blue shift of the PL peaks against the absorption edges, which indicates less trap density of the samples at lower fabrication voltage. Furthermore, in the PL measurement (Figure 4) without HTL, there was only a very slight decrease of the peak intensity for the sample when the second half-wave became more negative. In contrast, when HTL was mounted above the perovskite layer, the PL intensity has more greatly decreased compared to the ones without HTL at the same voltage, and it continuously decreased with more negative voltage of the second half-wave. This big difference with and without HTL has suggested a more significant influence of the voltage modulation on the hole transport other than on the electron transport. This decrease of the PL peak versus negative voltage is likely to be either attributed to fewer radiative recombination centers or to faster carrier motions due to enhanced transport ability of the perovskite material. This has also been supported by the TRPL measurement (details can be found in Table S3, Supporting Information). Under more negative voltage of second half-wave, the PL decays became gradually faster without HTL, with lifetime decreasing from 68.29 to 61.14 ns when voltage decreased from -0.5 to -2.5 V. This tendency has become more significant for the samples with HTL on top, where the lifetime dropped drastically from 35.91 to

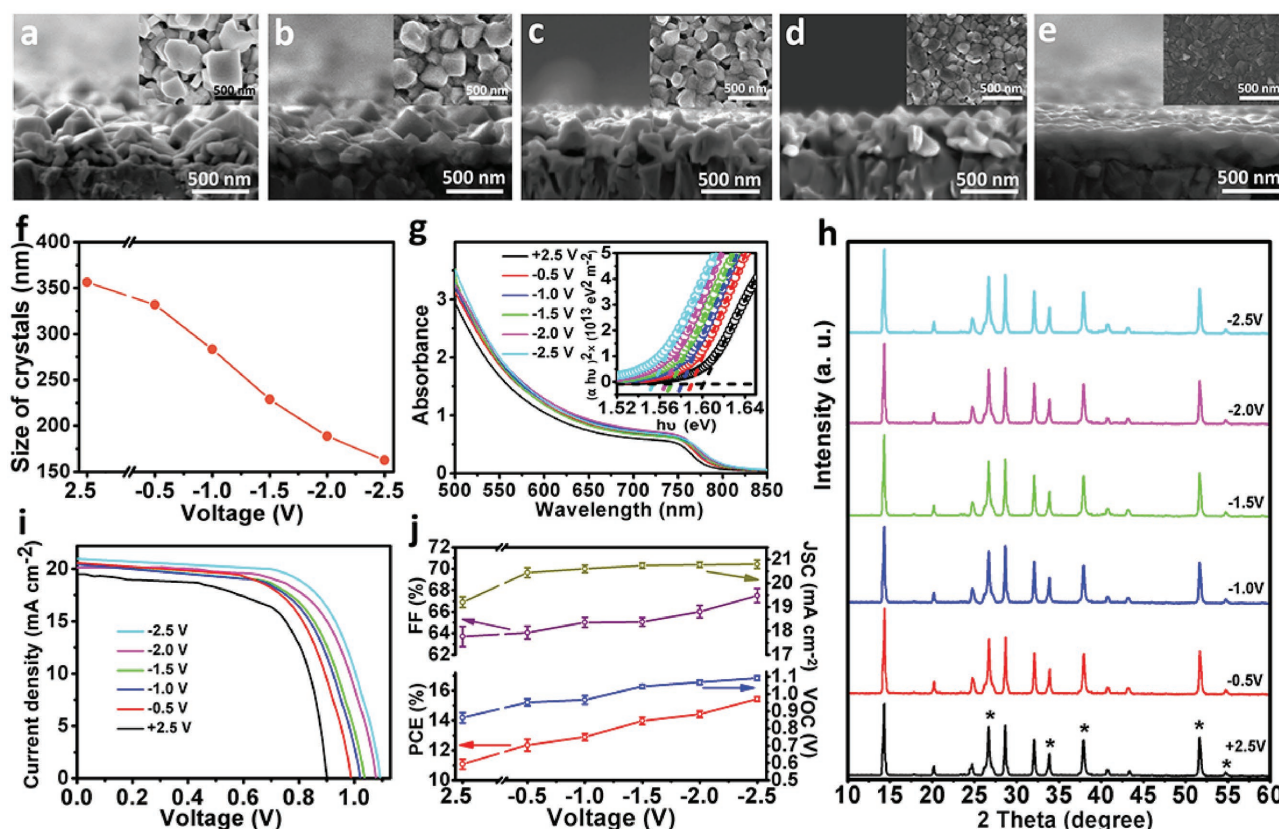


Figure 4. Characterization and dependence of MAPbI₃ film morphology on square-wave AC voltage with different second half-wave amplitude. SEM top view and cross-sectional view images of MAPbI₃ films prepared by square-wave AC voltage ($f = 5$ Hz) with different amplitude of second half-wave a) -0.5 V, b) -1.0 V, c) -1.5 V, d) -2.0 V, and e) -2.5 V, insets showing the top view. f) Size of MAPbI₃ grains at different voltage. The point at $+2.5$ V corresponds to potentiostatic condition. g) Absorption spectroscopy of samples at different voltage. h) XRD of samples vs voltage; the symbols “*” represent the peaks of FTO/c-TiO₂ substrate. i) Representative J - V characteristics and j) corresponding photovoltaic parameters of as-fabricated PSCs. The perovskite deposition time was kept at 5 min.

9.56 ns, again indicating hole-dominating carrier transport in the perovskite and better carrier transport under lower voltage.

Furthermore, unlike the Pb modulation, the EIS measurement in Figure 5e has demonstrated a significant decrease of the series resistance versus a more negative second half-wave of the controlling voltage. Significant change has also been

found in the two arcs, which have shown reduced contact resistance R_{co} and higher recombination resistance R_{rec} versus the decreasing controlling voltage, respectively. Therefore, it appears that the modulation of the second half-wave in step 2 has not only induced less recombination in the as-fabricated perovskite but also better carrier transport ability in the

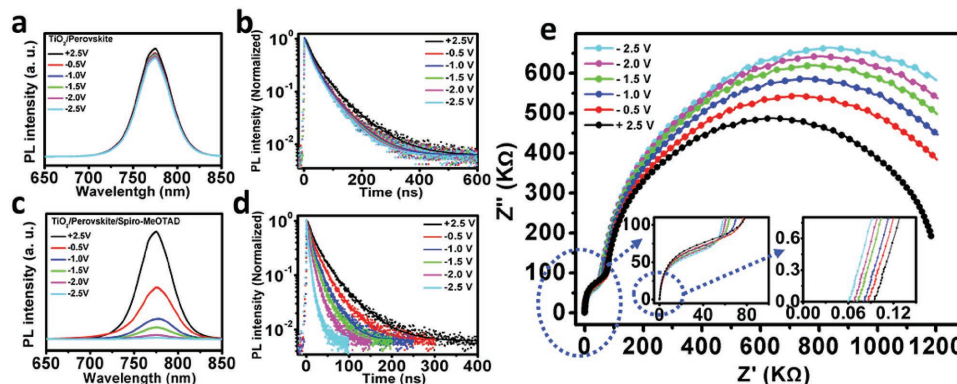


Figure 5. Optoelectronic properties of sample fabricated under different voltages. a,b) PL and TRPL of samples without spiro-MeOTAD on top of perovskite, respectively. c,d) PL and TRPL of samples with spiro-MeOTAD on top of perovskite, respectively. e) EIS measurements of PSCs fabricated at different voltage.

as-fabricated perovskite layer and the interfaces between different layers.

2.4. Time Evolution of Perovskite Formation

Remarkably, the sample surface has turned dark at the very beginning (just a few seconds) with the application of bias (potentiostatic or AC) in the perovskite formation in step 2. Therefore, the formation of perovskite in this electrochemical system should be a very fast process. A time-dependence experiment then became necessary for more details. For simplification, we have kept the frequency constant at 5 Hz, and the total growth time varied from 1 to 180 s. The morphological and structural change was monitored by scanning electron microscope (SEM) and XRD at different time steps in Figure 6. Starting from a bare c-TiO₂ surface with Pb islands (Figure 6a), a thin layer appeared around relatively higher islands at the very beginning (Figure 6b, 1 s), where the thin layer and the islands should be assigned to perovskite between Pb particles and perovskite-covered Pb islands, respectively. Afterward, the as-formed layer has become thicker, from about 220 to 370 nm (with details shown in Figure S9, Supporting Information), and the islands gradually disappeared until finally a totally flat layer was formed (Figure 6c–h). In the XRD patterns, the peaks of FTO/c-TiO₂ substrates were also recorded for comparison (Figure 6i). After electrodeposition in the first step, new peaks

appeared at 31.4°, 36.4°, and 52.6°, which are assigned to [111], [200], and [220] of lead crystal planes, corresponding to the data in JCPDS Card No. 6-0686. In the second step, the characteristic peaks of Pb became significantly weaker at 1 s, while the peaks at 14.2°, 20.0°, 24.6°, 28.5°, 31.9°, 40.6°, and 43.2° emerged, corresponding to the [110], [200], [202], [220], [310], [224], and [314] lattice planes of MAPbI₃, respectively. When the reaction went on to 120 s, as shown in Figure 6i, the characteristic peaks of Pb totally vanished and the peaks of MAPbI₃ were continuously strengthened, which is consistent with morphological evolution mentioned above. For the time longer than 120 s, the change of the characteristic peaks became trivial. This indicated that the previous reaction time of 5 min had been in fact beyond necessity and 120 s was seemingly enough for formation of adequate perovskite.

Furthermore, the time evolution of the elemental components of the sample was measured together with the corresponding PSC performance, as shown in Figure 6j (the EDS measurement can be found in Table S4, Supporting Information). The elemental analysis has indicated that the ratio of I versus Pb has drastically increased from 0:1 to 0.59:1 at 1 s, and then gradually increased to 2.68:1 at 60 s, with the rate of increase slowed down versus time. At 120 s, this ratio reached 3:1 and remained constant. It suggested that this process had a very fast initial growth of perovskite content at the beginning of the reaction and the Pb content was gradually converted to perovskite via reaction with MA⁺ and I[−] until finally all Pb was

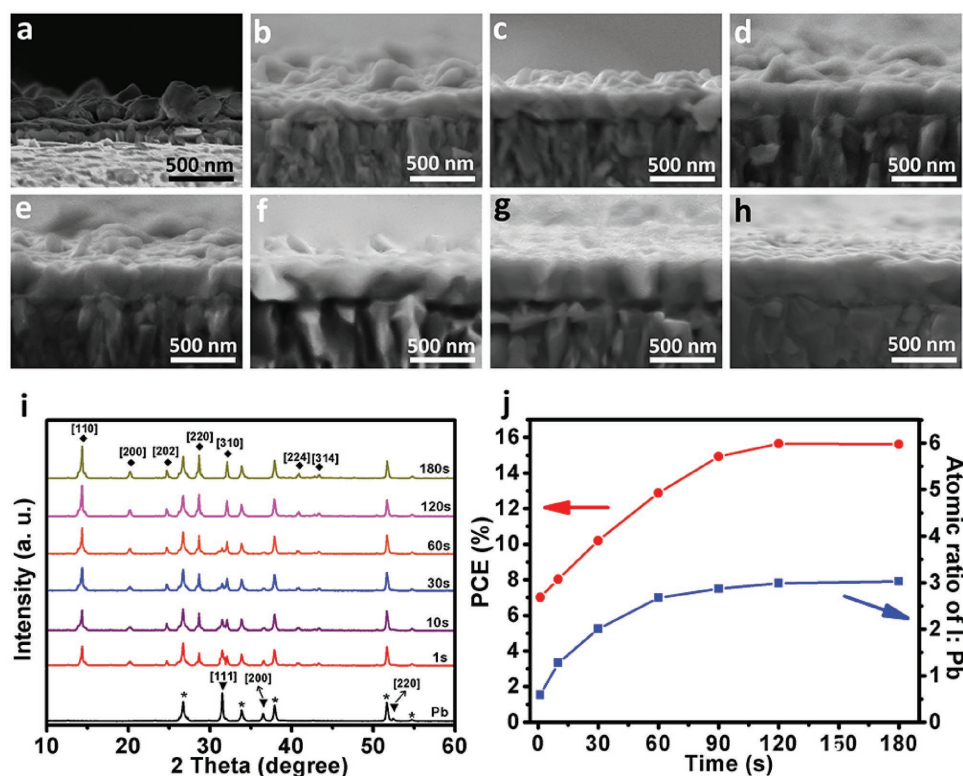


Figure 6. Time evolution of morphology, structure, element ratio, and device performance of MAPbI₃ perovskite in step 2. SEM cross section of samples grown at different time a) 0, b) 1, c) 10, d) 30, e) 60, f) 90, g) 120, and h) 180 s. i) XRD pattern of samples at 0–180 s, with symbols ▽, ◆, and * representing the peaks of Pb film, perovskite film, and FTO/c-TiO₂ substrate, respectively. j) Atomic ratio of I:Pb in perovskite and PCE of corresponding devices at each time point in step 2.

converted into perovskite and the total ratio of I:Pb became 3:1, exactly the same ratio in MAPbI_3 . The decreased value of curve slope in Figure 6j indicates that the growth of MAPbI_3 has become slower and slower versus time. The XRD and SEM series have further exhibited that perovskite has been continuously formed from both upper and bottom side of the initial perovskite layer simultaneously after it was first established around the Pb particles, otherwise visible vacancies can be observed with the consumption of Pb with the growth and flattening of the perovskite layer. This indicates that the bottom-up diffusion of Pb^{2+} and top-down diffusion of MA^+ through the initial perovskite layer have simultaneously existed. This may have explained the significant deceleration of perovskite growth in the later growth. As a result, at 120 s, the perovskite layer has exhibited homogeneous thickness around 375 nm and quite uniform grain size of about 170 nm, which would be suitable for later PSC integration.

2.5. Performance, Mechanism Study, and Outlook

According to previous investigations, the optimized conditions for the current system would be with -20 V pulse at 1 s and -2.5 V bias for 5 min in step 1 and then a 5 Hz AC bias for 2 min. As shown in Figure 7, corresponding PSC with a FTO/c- TiO_2 /perovskite/spiro-MeOTAD/Au architecture has exhibited a best PCE of 15.65% (reverse sweeping), with $V_{\text{OC}} = 1.098$ V, $J_{\text{SC}} = 20.99 \text{ mA cm}^{-2}$, and $\text{FF} = 67.91\%$. The parameters of forward sweeping were only slightly lower (with $\eta = 14.84\%$, $V_{\text{OC}} = 1.073$ V, $J_{\text{SC}} = 20.93 \text{ mA cm}^{-2}$, and $\text{FF} = 66.10\%$), indicating a quite low hysteresis (Figure 6a),^[51] and the corresponding external quantum efficiency (EQE) spectrum is shown in Figure 6b. The integrated response under standard reference spectrum was 20.97 mA cm^{-2} , which is close to the J_{SC} measured by the simulator. Efficiency statistics of all samples are presented in Figure 7c, exhibiting an average power

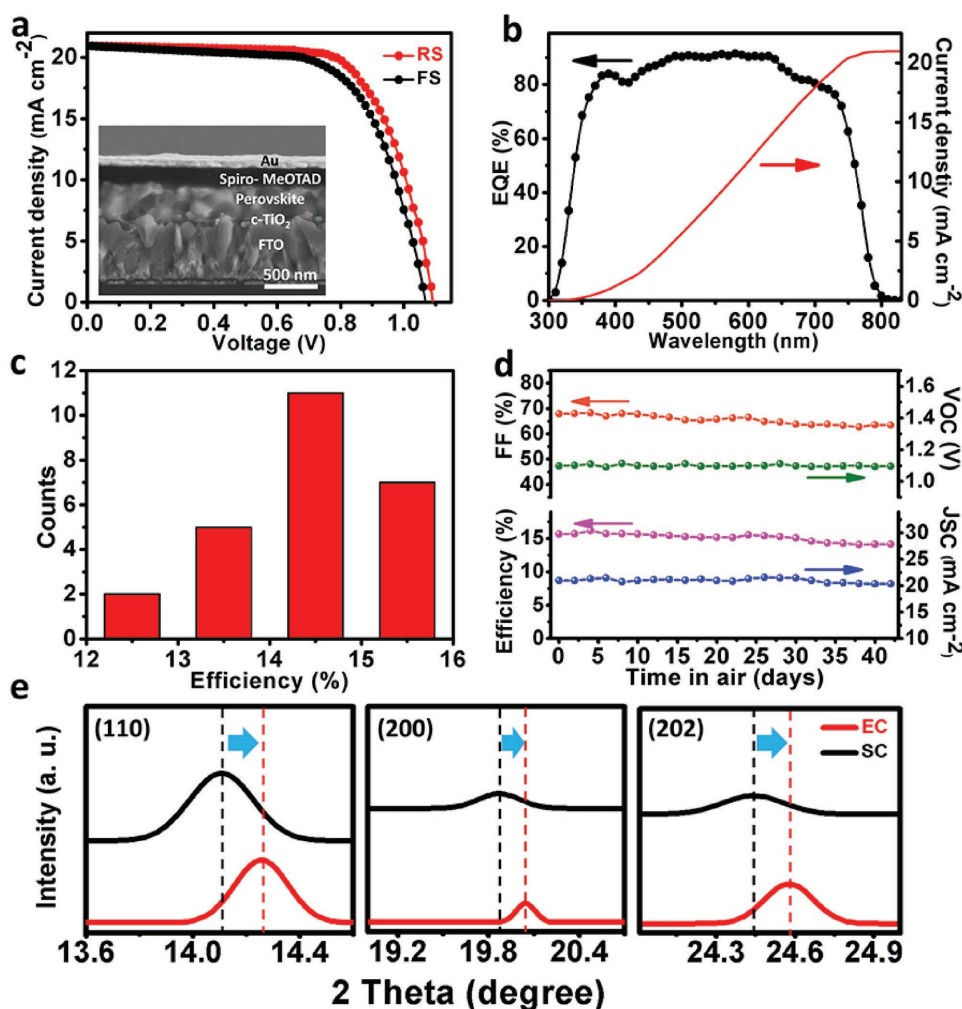


Figure 7. Characteristics of electrodeposited MAPbI_3 perovskite solar cells. a) J - V curves of the optimized electrodeposited MAPbI_3 PSC, insets showing the SEM cross-sectional view of the device. b) Corresponding EQE of the optimized PSC. c) Efficiency statistics of the electrodeposited MAPbI_3 PSCs under optimized conditions. d) Photovoltaic parameters variation of PSCs with number of days stored in air at about 25°C with 20%–40% relative humidity. e) Details for characteristic XRD peaks of electrochemically fabricated sample compared to spin-coating fabricated sample, with the shift marked by the arrows. EC and SC stand for electrochemically fabricated sample and spin-coating fabricated sample, respectively.

conversion efficiency of $14.52 \pm 0.88\%$, which demonstrates a splendid reproducibility of cells. Additionally, taking into account the spectral mismatch factor of the reference Si cell ($M = 1.003$), the spectral mismatch factor of perovskite cell in this work was about 0.998, which means the exact performance of the cell can be slightly higher.^[52]

Furthermore, as has been normally evaluated for perovskites, the stability of unsealed devices fabricated with the electrodeposited perovskite films was also evaluated in a typical 42 d (≈ 1000 h) long-term measurement.^[53] The as-fabricated PSCs were stored in air under ambient temperature of about 25 °C with relative humidity of 20%–40%, taken out and measured in atmosphere every 2 d, with their performance change being summarized in Figure 8d (J – V curves can be found in Figure S10, Supporting Information). The overall efficiency loss over 42 d was 9.8% (from 15.65% to 14.11%). Especially, the loss was very little (from 15.65% to 15.53%, about 0.7%) in the first 24 d, which indicated quite good stability. Considering the period of measurement was the rainy and humid season in Shanghai (normally 80–100 RH%), the true stability is even higher. Interestingly, the J_{SC} has slightly increased during the initial period of storage, leading to PCE increase, too.

Recently, a number of reports have achieved remarkable results in the stability study, with main routes through either shielding protection by treatment of layers outside perovskite^[54–56] or additional implanted materials inside the perovskite.^[57] In this work, the sample exhibited enhanced stability without shielding or implant and only by modulation of the layer itself. However, the origin of such stability still remains unknown. Hence, we have carried out further studies on the material first by X-ray reflectivity (XRR) measurement. Though with possible error, XRR results indicate significantly higher density (5.24 g cm^{-3}) of the electrochemically fabricated perovskite compared to the control sample (4.49 g cm^{-3}) fabricated by conventional two-step chemical method. Moreover, detailed study on the XRD has shown significant shift of the characteristic peaks toward larger angle compared to the control sample, which indicates certain lattice contraction in this electrochemically fabricated sample. For instance, as shown in Figure 7e, the positions of [110], [200], and [202] peaks of the sample by electrochemical method are 14.23° , 20.04° , and 24.58° , while these values are 14.08° , 19.91° , and 24.46° for normal spin-coated sample. The corresponding lattice constants are $a = 8.851 \text{ \AA}$, $b = 8.734 \text{ \AA}$, $c = 12.552 \text{ \AA}$, and $a = 8.908 \text{ \AA}$, $b = 8.862 \text{ \AA}$, $c = 12.579 \text{ \AA}$ for the electrochemical samples and spin-coating samples, respectively. Besides, the FWHM of those peaks has also become narrower under electrochemical condition (shown in Figure 7e, detailed value can be found in Table S5, Supporting Information), suggesting more ordered crystallization in the electrochemical process compared to two-step chemical growth. Considering these facts together with the

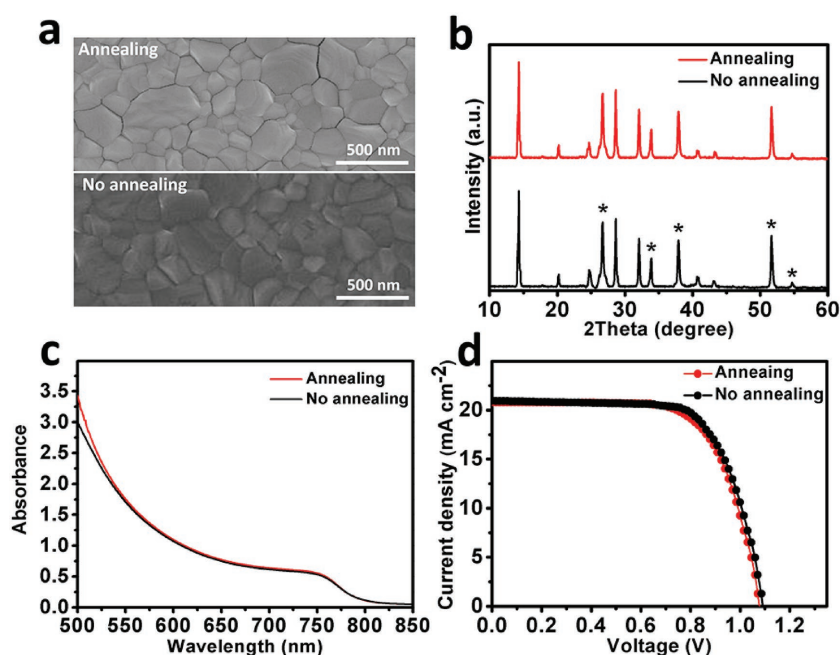


Figure 8. Characterization of the electrodeposited MAPbI₃ perovskite films and corresponding PSCs with and without thermal annealing. a) Top view SEM images of electrodeposited perovskite films with annealing at 70 °C for 30 min (bottom) and without annealing (top). b) Corresponding XRD patterns. c) UV–vis absorption spectra. d) J – V curves of as-fabricated PSC devices. The symbols (*) represent the peaks of FTO/c-TiO₂ substrate.

enhancement of stability, it implies that the lattice contraction with better ordering and more compactness of the perovskite film are the more probable origin of the enhanced stability, which can in some degree limit the motion of ions (such as methylammonium cations) that has been accepted as one key factor for the chemical instability (with polar solvents such as water) according to previous studies on the stability.^[31] This phenomenon can possibly be induced by the extra force from the electric field and the heat from the electrochemical process, which offers more activation energy for the lattice formation. For the initial increase of efficiency, one possible origin of this phenomenon is the reduced charge traps in the bulk of perovskite films due to the water molecule healing effect on perovskite film according to some other groups.^[16,58–60]

Besides morphological and structural behavior influenced by the electrochemical parameters, it is also noticeable that all the efficiencies of the PSCs were obtained without thermal annealing, which has been a standard process for post-treatment prior to PSC fabrication in almost all existing methods. To investigate this, we have carried out control experiments with thermal annealing (70 °C for 30 min) after the formation of the electrodeposited perovskite under the same conditions. Figure 8 shows another sample using optimized conditions, which has indicated no significant change in the morphology, structure, and UV–vis absorbance of the thermally annealed sample compared to the one without thermal annealing. The parameters of the as-fabricated PSCs shown in Figure 8d were $\eta = 15.62\%$ (with $V_{OC} = 1.086 \text{ V}$, $J_{SC} = 20.91 \text{ mA cm}^{-2}$, and $FF = 68.78\%$) and 15.17% (with $V_{OC} = 1.077 \text{ V}$, $J_{SC} = 20.77 \text{ mA cm}^{-2}$, and $FF = 67.82\%$) before and after thermal annealing, respectively (also

very close). Therefore, we can conclude that conventional thermal annealing would not be necessary for the sample in this method, which has shown adequate quality as-fabricated.

This result suggests that the as-fabricated perovskite has already been well-crystallized directly after the electrodeposition, which could be explained by a possible current annealing effect by the electrochemical process, that is to say, the electric field can offer extra energies for the activation energy of the lattice formation from amorphous state to crystallized one.^[39] A similar phenomenon has also been found in other systems such as the anodic oxidation of TiO₂ nanotubes.^[40] Additionally, there was even a little decrease of V_{OC} on the PSC fabricated with annealed perovskite film (Figure 8d), which might be induced by thermal expansion due to heating and current annealing and thus increased the separation between grains.

Until now, though results have clearly demonstrated effective growth of perovskite and significant improvement of both the layer quality and the interfacial conditions, questions still arise about a general picture of the perovskite formation. Though limited by resolution, some information can still be given by the EDS surface scanning technique on the formation process, as shown in Figure 9a–c. In the beginning (1 s), the distribution of I and Pb does not entirely overlap each other, indicating incomplete formation of a perovskite layer. In the middle of reaction (60 s), it can be seen that a layer has been established where I and Pb components have similar distribution, with

only some difference on a few islands. In this stage, a complete perovskite layer is almost formed. At the end (120 s), I and Pb are homogeneously distributed in the whole formed layer. This is well consistent with the time series study in Section 2.4 by XRD and total elemental measurement.

More interesting phenomena can be found by further looking into the J - t curves of the electrochemistry station during the perovskite fabrication (Figure 9d). In general, the current has shown oscillating behavior throughout the process. With the oscillation period following the voltage oscillation (± 2.5 V, 5 Hz), the value of its peaks and valleys varies during the growth. Following an initial slight increase in the first few seconds (about 3 s), the extreme values of current gradually decreased during the growth, and was almost constant at about 120 s. The time scale of the initial increase of the extreme values is well consistent with the formation of the initial perovskite layer indicated in Figure 9a. Since the total current in the solution is attributed to both anions and cations, it indicates a stage of direct combination of ionic species being intensified as more MA⁺ and I⁻ arrived at the Pb surface by electric drift so that the sum charge transfer is enhanced. However, after this initial thin layer is established, the ions have to pass through the thicker and thicker layer before the reaction and the amount of Pb also decreased due to consumption. Therefore, the average current has followed a general decrease. The time of 120 s, when oscillation becomes stable, is quite consistent

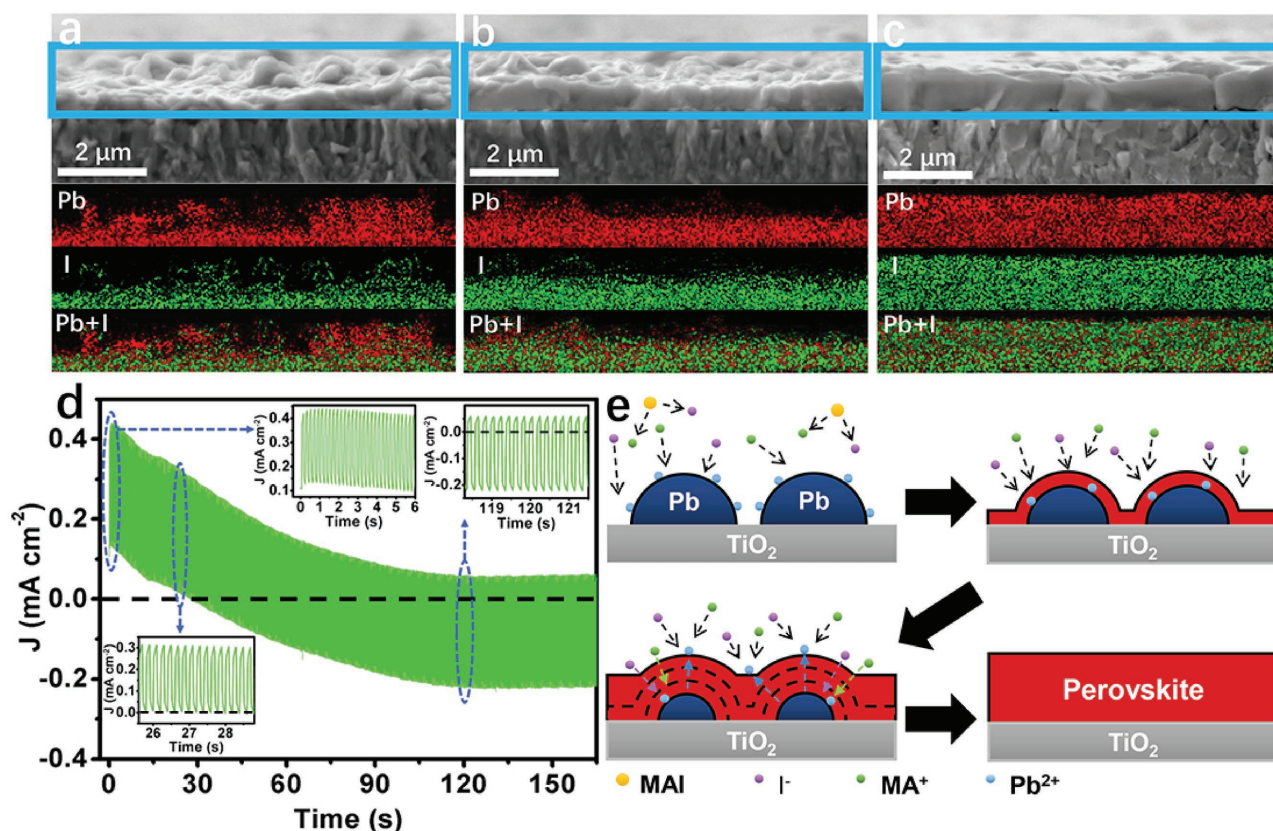


Figure 9. Investigation on the formation process of perovskite. a–c) EDS surface scanning of the sample in different characteristic time stages: a) 1, b) 60, and c) 120 s. d) J - t characteristics of the perovskite formation procedure, with the insets demonstrating three different time stages of the formation, AC ± 2.5 V. e) A brief description of the growth procedure.

with the optimized time of perovskite growth mentioned in Section 2.4, which can be easily understood because all Pb has been consumed.

Another interesting phenomenon is the significant asymmetric behavior of the current oscillation in the reaction, especially within the initial 27 s when all current remained positive, demonstrating a diode-like behavior or so-called “ion current rectification” (ICR) in the solution.^[61,62] According to related studies, this phenomenon has suggested certain charge accumulation that has emerged due to the ion motion and induced screening effect that can influence the ionic current. Considering the positive polarity of the current, the most probable candidate would be the Pb^{2+} . After 120 s, the oscillation became stable and the negative current became larger, where anions should play the main role instead. For more information, we have measured the concentration change of the chemical contents in the electrolyte near the electrode by inductively coupled plasma (ICP) emission spectroscopy. On the one hand, Pb concentration near the substrate (working electrode) was quite high in the beginning (29.44 ppm, 10 s) and rather low at 120 s (0.5615 ppm), while there was only slight enrichment near the counter electrode (0.08751 ppm at 10 s to 0.4277 ppm at 120 s) during the whole process. On the other hand, the concentration of iodine is at least two orders of magnitude higher than the Pb concentration near the substrate and four orders of magnitude higher near the counter electrode (can be found in Table S7, Supporting Information). Considering the ICR phenomenon at an early stage, this indicates that only a small part of iodine is in the ionic form and the ionization of MAI should be quite stable since the current oscillation was stable after 120 s. The quite low Pb concentration near the counter electrode also indicates that the moving distance of Pb^{2+} should be much shorter than I^- species in the solution, which can also be supported by the significant decrease of iodine near the counter electrode. Most Pb^{2+} should react immediately with MAI^+ and I^- after they were accumulated near the substrate. After 120 s,

when all Pb has been consumed, I^- becomes dominant in the ionic current; the more negative current in the oscillation has suggested possible MAI^+ accumulation near the counter electrode, as they have been ionized from MAI simultaneously with I^- .

Eventually, we can draw a brief picture on the electrochemical fabrication of perovskite in the following steps (Figure 9e): (1) Formation of ionic species, that is, the Pb^{2+} by oxidation of Pb by positive bias (fast process) and MAI^+ as well as I^- by ionization process in isopropanol solution (slow but stable process); (2) Initial formation of a thin perovskite layer around the Pb nuclei and on the TiO_2 substrate among the Pb nuclei by direct reaction of Pb ions and methylammonium cations; (3) Continuous growth of perovskite both above the initial layer and below the layer, where the ions have to pass through the already formed perovskite layer by thermal diffusion and drift by the electric field; and (4) Finally, the Pb is all converted into perovskite. Studying the ionic process and layer formation might be helpful for possible further optimization and development, for example, one-step electrochemical fabrication. Besides, the flattening of perovskite layer by negative second half-wave can be possibly due to more homogeneous Pb^{2+} distribution with more lateral diffusion under such AC conditions, which would require advanced in situ monitoring techniques and systematic theoretical studies.

Finally, it has been found that the electrochemical method in this work has shown a significant advantage in making homogeneous deposited film compared to conventional methods based on spin-coating techniques, as have also been indicated by other pioneer works.^[34–36] It can also be seen from Figure 1, where the original sample has size over 2 cm^2 . To test that for this investigation, we have used large-scale samples according to the size limit of our current testing platform. As shown in Figure 10 on the tested area of 2 cm^2 , the sample has an efficiency of 10.45% (reverse scanning) and 9.03% (forward scanning) with FF over 0.59. This result is comparable with some

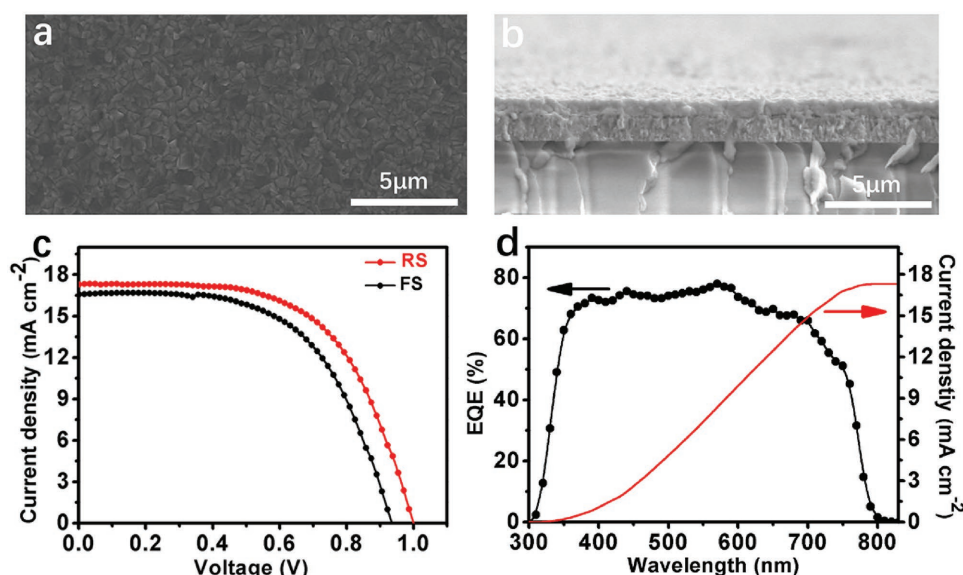


Figure 10. Large cell (effective area 2 cm^2) by electrochemical method in this work. a,b) Top and cross-sectional view of the sample morphology under SEM, respectively. c) J - V characteristics and d) EQE of the as-fabricated cell.

previous results obtained by the spin-coating method with smaller effective area (1 cm^2 by pure spin-coating on $\text{TiO}_2^{[63]}$ and 0.07 mm^2 by spin-coating on electrodeposited substrate^[36]). With introduction of larger counter electrode, better results can still be expected for larger scales.

3. Conclusion

Results of this work have clearly demonstrated that multiple component perovskite materials can be effectively fabricated via ionic reaction under modulated electric fields applied to targeted substrate. Further study on the absorption spectra, PL, TRPL, and EIS of the samples has revealed rather low trap state and good conductivity of the carriers, in the meantime with no need of conventional thermal annealing. The as-fabricated samples have also exhibited high long-term stability. Hopefully, the same method can easily be applied to other types of perovskite on different substrates as well (for instance, nanoporous TiO_2 and ZnO). The growth of perovskite under electric field is a very fast process, although the complete conversion of Pb into perovskite can be more slowly due to diffusion control of reactive ions in the pre-formed perovskite layer between the Pb precursor and electrolyte. Nevertheless, combining step 1 and 2 together may resolve this issue by direct reaction of ionic species continuously at the surface. In general, with further physical/chemical modulation, wider applications can be expected in the future development—not only in the development of the examples given in this work (roll-to-roll fabrication, etc.) but also in fabrication of other solar cells such as perovskite/Si tandem cells and other optoelectronic devices.

4. Experimental Section

Preparation of Substrate: The FTO glass (Materwin, $14 \Omega \text{ sq}^{-1}$) was cleaned sequentially via detergent, water, acetone, isopropanol, and ethanol under ultrasonication for 15 min. The c- TiO_2 electron conducting layer was prepared on the FTO glass by standard sequential procedures consisting of 30 s spin-coating of titanium diisopropoxide bis(acetylacetonate) solution (Materwin, 0.15 M, in 1-butanol) at 4000 rpm, drying at 125°C for 5 min, repeating twice with 0.3 M titanium diisopropoxide bis(acetylacetonate) solution (Materwin, 0.3 M, in 1-butanol), and a final heating at 500°C for 15 min. The resultant film was immersed into a $40 \times 10^{-3} \text{ M}$ TiCl_4 aqueous solution at 70°C for 30 min, washed with deionized water and ethanol, and then baked at 500°C for 15 min.

Electrochemical Fabrication of Perovskite: The electrodeposition of perovskite was performed in a two-electrode cell equipped with the c- TiO_2 coated FTO glass working electrode and a Pt counter electrode. The electric parameters were controlled by an electrochemical station (Corrtest, CS350) together equipped with voltage amplifier (Corrtest, CS1006). The first step of Pb deposition was carried out in the electrolyte consisting of isopropanol solutions of $10 \times 10^{-3} \text{ M}$ PbI_2 (Sigma-Aldrich, 99.99%), 1.3 M sodium iodide (NaI, Aladdin reagent, 99.99%), and $700 \times 10^{-3} \text{ M}$ ethylene glycol tertiary butylether (ETB, Aladdin reagent, 99%). The resultant films were then rinsed with isopropanol and dried with N_2 flow. The second step of perovskite formation was performed in the electrolyte of isopropanol solution of MAI (10 mg mL^{-1}). The products were rinsed with isopropanol and dried with N_2 flow in nitrogen protection. The reaction was protected by N_2 in the chamber of the cell and kept under room temperature.

Fabrication of Perovskite Solar Cells: The HTM was then deposited on the as-formed samples by spin-coating at 4000 rpm for 30 s. The spin-coating formulation was prepared by dissolving 72.3 mg spiro-MeOTAD, 28.8 μL 4-*tert*-butylpyridine (Aladdin reagent, 96%), 17.5 μL acetonitrile solution (520 mg mL^{-1}) of lithium bis(trifluoromethylsulfonyl)imide (Aladdin reagent, 99%), and 29 μL acetonitrile solution (300 mg mL^{-1}) of tris(2-(1H-pyrazol-1-yl)-4-*tert*-butylpyridine)-cobalt(III) tris(bis(trifluoromethylsulfonyl)imide) (FK209, Materwin, 99%) in 1 mL chlorobenzene (Aladdin reagent, 99.9%). Finally, 80 nm Au was thermally evaporated on top of HTM in vacuum as the upper electrode of the solar cell.

Characterization of Materials and Devices: The morphology of the samples was observed by field-emission scanning electron microscope (FESEM, Zeiss Ultra Plus). The elemental analysis was measured by the EDS installed in the SEM system (Oxford Instruments, Aztec X-Max 20). The absorption spectra of the MAPbI_3 perovskite film on c- TiO_2 coated FTO were measured by an ultraviolet–visible spectrophotometer (Lambda 20 spectrophotometer, Perkin-Elmer, USA) in the 400–850 nm wavelength range at room temperature. The structural information was examined by XRD via an X-ray polycrystalline diffractometer (D8 Advance Da Vinci, Bruker, Germany). The XRR measurements were carried out in Shanghai Synchrotron Radiation facility (SSRF, China) with a wavelength $\lambda = 0.691356 \text{ \AA}$. The beam was reduced in the reflectivity plane by $50 \mu\text{m}$ wide slits in order to minimize the irradiated footprint at the sample position. After careful adjustments of the sample, data were collected from 0° to 1° of critical angle with a 0.005° step and corrected from irradiated area. The ICP emission spectroscopy of I and Pb was measured with ICP optical emission spectrometer (iCAP6300, Thermo, USA) and ICP mass spectrometer (Agilent 7500a, Agilent, USA), respectively.

The size of all perovskite solar cells was $2 \text{ cm} \times 2 \text{ cm}$, with an active area of 0.15 cm^2 defined by the mask covered on the cell. The steady-state PL was measured by Horiba Jobin Yvon system (France) with excitation at 514.5 nm using an argon ion laser. The TRPL measurement was carried out using time-resolved fluorescence spectrofluorometer (Horiba Jobin Yvon, FL, Japan). The samples were excited by a pulsed laser (NanoLED-460, Horiba Jobin Yvon, FL, Japan) with a wavelength and pulse width of 460 nm and 1.3 ns, respectively. The PL photons were counted by DAM302 (Horiba Jobin Yvon, FL, Japan). The EIS measurements were carried out with an electrochemical station (Corrtest, CS350) under dark condition. The devices were held at their respective open circuit potentials obtained from the J - V measurements with an oscillating voltage of 10 mV and frequency of 1 Hz to 1 MHz, while the EIS spectrum was being recorded. The EIS spectra were fitted by Zview software.

The J - V characteristics of the perovskite solar cells were measured by a computer-programmed electronic sourcemeter (Keithley, 2400) with a standard Solar Simulator (Newport, Oriel Sol-2A) under 1 sun AM 1.5. The scanning voltage ranged from -0.3 to 1.2 V (forward) and 1.2 to -0.3 V (backward), respectively. The solar cells were measured as-prepared without any post-treatment. The scanning rate and time delay were 0.15 V s^{-1} and 10 ms, respectively. A standard reference Si solar cell (effective area $2 \times 2 \text{ cm}^2$, certified by VLSI Standards Inc.) was applied for calibration of simulator and calculation for spectral mismatch, with its own mismatch factor $M = 1.003$. The EQE spectrum was measured by a Quantum Efficiency/IPCE system (PV Measurements Inc., QEX10) in the 300–850 nm wavelength range at room temperature. During the stability measurement, the cells were stored simply in a box desiccated by silica gel and kept at room temperature and relative humidity of about 20%–40%. The PSCs were taken out for measurement every 2 d.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

F.Z. and H.L. contributed equally to this work. This work was supported by the Natural Science Foundation of China (61234005, 11204176, and 11474201) and the National Major Basic Research Project (2012CB934302).

Received: November 21, 2016

Revised: December 20, 2016

Published online:

- [1] S. D. Stranks, G. E. Eperon, G. Grancini, C. Menelaou, M. J. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza, H. J. Snaith, *Science* **2013**, 342, 341.
- [2] Q. Dong, Y. Fang, Y. Shao, P. Mulligan, J. Qiu, L. Cao, J. Huang, *Science* **2015**, 347, 967.
- [3] F. Hao, C. C. Stoumpos, D. H. Cao, R. P. H. Chang, M. G. Kanatzidis, *Nat. Photonics* **2014**, 8, 489.
- [4] D. P. McMeekin, G. Sadoughi, W. Rehman, G. E. Eperon, M. Saliba, M. T. Höranter, A. Haghighirad, N. Sakai, L. Korte, B. Rech, *Science* **2016**, 351, 151.
- [5] A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, *J. Am. Chem. Soc.* **2009**, 131, 6050.
- [6] M. Z. Liu, M. B. Johnston, H. J. Snaith, *Nature* **2013**, 501, 395.
- [7] J. Burschka, N. Pellet, S. J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin, M. Grätzel, *Nature* **2013**, 499, 316.
- [8] W. Li, J. Fan, J. Li, Y. Mai, L. Wang, *J. Am. Chem. Soc.* **2015**, 137, 10399.
- [9] J. H. Heo, S. H. Im, J. H. Noh, T. N. Mandal, C.-S. Lim, J. A. Chang, Y. H. Lee, H.-j. Kim, A. Sarkar, M. K. Nazeeruddin, M. Grätzel, S. I. Seok, *Nat. Photonics* **2013**, 7, 486.
- [10] J. H. Im, I. H. Jang, N. Pellet, M. Grätzel, N. G. Park, *Nat. Nanotechnol.* **2014**, 9, 927.
- [11] G. E. Eperon, V. M. Burlakov, P. Docampo, A. Goriely, H. J. Snaith, *Adv. Funct. Mater.* **2014**, 24, 151.
- [12] Q. Chen, H. Zhou, Z. Hong, S. Luo, H. S. Duan, H. H. Wang, Y. Liu, G. Li, Y. Yang, *J. Am. Chem. Soc.* **2014**, 136, 622.
- [13] Y. Z. Wu, A. Islam, X. D. Yang, C. J. Qin, J. Liu, K. Zhang, W. Q. Peng, L. Y. Han, *Energy Environ. Sci.* **2014**, 7, 2934.
- [14] H. Zhang, J. Mao, H. He, D. Zhang, H. L. Zhu, F. Xie, K. S. Wong, M. Grätzel, W. C. H. Choy, *Adv. Energy Mater.* **2015**, 5, 1501354.
- [15] H. Zhou, Q. Chen, G. Li, S. Luo, T.-B. Song, H.-S. Duan, Z. Hong, J. You, Y. Liu, Y. Yang, *Science* **2014**, 345, 542.
- [16] Y. Deng, Q. Dong, C. Bi, Y. Yuan, J. Huang, *Adv. Energy Mater.* **2016**, 6, 1600372.
- [17] N. Ahn, D. Y. Son, I. H. Jang, S. M. Kang, M. Choi, N. G. Park, *J. Am. Chem. Soc.* **2015**, 137, 8696.
- [18] X. Li, M. I. Dar, C. Yi, J. Luo, M. Tschumi, S. M. Zakeeruddin, M. K. Nazeeruddin, H. Han, M. Grätzel, *Nat. Chem.* **2015**, 7, 703.
- [19] N. J. Jeon, J. H. Noh, Y. C. Kim, W. S. Yang, S. Ryu, S. I. Seok, *Nat. Mater.* **2014**, 13, 897.
- [20] E. Edri, S. Kirmayer, S. Mukhopadhyay, K. Gartsman, G. Hodes, D. Cahen, *Nat. Commun.* **2014**, 5, 3461.
- [21] Y. Ma, L. Zheng, Y. H. Chung, S. Chu, L. Xiao, Z. Chen, S. Wang, B. Qu, Q. Gong, Z. Wu, X. Hou, *Chem. Commun.* **2014**, 50, 12458.
- [22] C. Tao, S. Neutzner, L. Colella, S. Marras, A. R. S. Kandada, M. Gandini, M. D. Bastiani, G. Pace, L. Manna, M. Caironi, C. Bertarelli, A. Petrozza, *Energy Environ. Sci.* **2015**, 8, 2365.
- [23] N. K. Noel, A. Abate, S. D. Stranks, E. S. Parrott, V. M. Burlakov, A. Goriely, H. J. Snaith, *ACS Nano* **2014**, 8, 9815.
- [24] F. Fu, T. Feurer, T. Jäger, E. Avancini, B. Bissig, S. Yoon, S. Buecheler, A. N. Tiwari, *Nat. Commun.* **2015**, 6, 8932.
- [25] M. Saliba, T. Matsui, J. Y. Seo, K. Domanski, J. P. Correa-Baena, M. K. Nazeeruddin, S. M. Zakeeruddin, W. Tress, A. Abate, A. Hagfeldt, M. Grätzel, *Energy Environ. Sci.* **2016**, 9, 1989.
- [26] NREL record solar cell efficiency table, http://www.nrel.gov/ncpv/images/efficiency_chart.jpg (accessed: April 2016).
- [27] F. Giordano, A. Abate, J. P. C. Baena, M. Saliba, T. Matsui, S. H. Im, S. M. Zakeeruddin, M. K. Nazeeruddin, A. Hagfeldt, M. Grätzel, *Nat. Commun.* **2016**, 7, 10379.
- [28] R. S. Sanchez, E. Mas-Marza, *Sol. Energy Mater. Sol. Cells* **2016**, DOI: 10.1016/j.solmat.2016.03.024.
- [29] H. S. Kim, N. G. Park, *J. Phys. Chem. Lett.* **2014**, 5, 2927.
- [30] L. L. Zheng, Y. H. Chung, Y. Z. Ma, L. P. Zhang, L. X. Xiao, Z. J. Chen, S. F. Wang, B. Qu, Q. H. Gong, *Chem. Commun.* **2014**, 50, 11196.
- [31] T. Leijtens, G. E. Eperon, N. K. Noel, S. N. Habisreutinger, A. Petrozza, H. J. Snaith, *Adv. Energy Mater.* **2015**, 5, 1500963.
- [32] B.-W. Park, S. M. Jain, X. Zhang, A. Hagfeldt, G. Boschloo, T. Edvinsson, *ACS Nano* **2015**, 9, 2088.
- [33] H.-A. Chen, M.-H. Lee, C.-W. Chen, *J. Mater. Chem. C* **2016**, 4, 5248.
- [34] J. H. Huang, K. J. Jiang, X. P. Cui, Q. Q. Zhang, M. Gao, M. J. Su, L. M. Yang, Y. L. Song, *Sci. Rep.* **2015**, 5, 15889.
- [35] X. P. Cui, K. J. Jiang, J. H. Huang, X. Q. Zhou, M. J. Su, S. G. Li, Q. Q. Zhang, L. M. Yang, Y. L. Song, *Chem. Commun.* **2015**, 51, 1457.
- [36] H. N. Chen, Z. H. Wei, X. L. Zheng, S. H. Yang, *Nano Energy* **2015**, 15, 216.
- [37] H. Fu, H. Liu, W. Shen, *Nanoscale Res. Lett.* **2014**, 9, 631.
- [38] L. Tao, Y. Xiong, H. Liu, W. Shen, *Nanoscale* **2014**, 6, 931.
- [39] Y. Xiong, L. Tao, H. Liu, W. Shen, *J. Mater. Chem. A* **2013**, 1, 783.
- [40] H. Liu, L. Tao, W. Z. Shen, *Electrochim. Acta* **2011**, 56, 3905.
- [41] O. Horváth, I. Mikó, *J. Photochem. Photobiol., A* **1998**, 114, 95.
- [42] A. Duleh, N. Tétreault, T. Moehl, P. Gao, M. K. Nazeeruddin, M. Grätzel, *Adv. Funct. Mater.* **2014**, 24, 3250.
- [43] B. Conings, L. Baeten, C. De Dobbelaere, J. D'Haen, J. Manca, H. G. Boyen, *Adv. Mater.* **2014**, 26, 2041.
- [44] Y. H. Kwon, S. K. Kim, S. W. Kim, H. K. Cho, *J. Electrochem. Soc.* **2014**, 161, D447.
- [45] *Luminescent Materials and Applications* (Ed: A. Kitai), Wiley, Chichester, England **2008**, p. 32.
- [46] J. B. You, Z. B. Hong, Y. M. Yang, Q. Chen, M. Cai, T. B. Song, C. C. Chen, S. R. Lu, Y. S. Liu, H. P. Zhou, Y. Yang, *ACS Nano* **2014**, 8, 1674.
- [47] J. X. Song, W. D. Hu, X. F. Wang, G. Chen, W. J. Tian, T. Miyasaka, *J. Mater. Chem. A* **2016**, 4, 8435.
- [48] K. Wang, Y. T. Shi, Q. S. Dong, Y. Li, S. F. Wang, X. F. Yu, M. Y. Wu, T. L. Ma, *J. Phys. Chem. Lett.* **2015**, 6, 755.
- [49] W. J. Ke, G. J. Fang, J. W. Wan, H. Tao, Q. Liu, L. B. Xiong, P. L. Qin, J. Wang, H. W. Lei, G. Yang, M. C. Qin, X. Z. Zhao, Y. F. Yan, *Nat. Commun.* **2015**, 6, 6700.
- [50] D. Q. Bi, A. M. El-Zohry, A. Hagfeldt, G. Boschloo, *ACS Appl. Mater. Interfaces* **2014**, 6, 18751.
- [51] M. Grätzel, *Nat. Mater.* **2014**, 13, 838.
- [52] H. J. Snaith, *Energy Environ. Sci.* **2012**, 5, 6513.
- [53] M. C. Beard, J. M. Luther, A. J. Nozik, *Nat. Nanotechnol.* **2014**, 9, 951.
- [54] T. Gatti, S. Casaluci, M. Prato, M. Salerno, F. D. Stasio, A. Ansaldo, E. Menna, A. D. Carlo, F. Bonaccorso, *Adv. Funct. Mater.* **2016**, 26, 7443.
- [55] F. Bella, G. Griffini, J.-P. Correa-Baena, G. Saracco, M. Grätzel, A. Hagfeldt, S. Turri, C. Gerbaldi, *Science* **2016**, 354, 203.

- [56] Z. Song, A. Abate, S. C. Watthage, G. K. Liyanage, A. B. Phillips, U. Steiner, M. Graetzel, M. J. Heben, *Adv. Energy Mater.* **2016**, 6, 1600846.
- [57] A. K. Baranwal, S. Kanaya, T. A. N. Peiris, G. Mizuta, T. Nishina, H. Kanda, T. Miyasaka, H. Segawa, S. Ito, *ChemSusChem* **2016**, 9, 2604.
- [58] D. Wang, M. Wright, N. K. Elumalai, A. Uddin, *Sol. Energy Mater. Sol. Cells* **2016**, 147, 255.
- [59] G. E. Eperon, S. N. Habisreutinger, T. Leijtens, B. J. Bruijns, J. J. van Franeker, D. W. deQuilettes, S. Pathak, R. J. Sutton, G. Grancini, D. S. Ginger, R. A. J. Janssen, A. Petrozza, H. J. Snaith, *ACS Nano* **2015**, 9, 9380.
- [60] W. Zhou, Y. Zhao, C. Shi, H. Huang, J. Wei, R. Fu, K. Liu, D. Yu, Q. Zhao, *J. Phys. Chem. C* **2016**, 120, 4759.
- [61] W.-J. Lan, M. A. Edwards, L. Luo, R. T. Perera, X. Wu, C. R. Martin, H. S. White, *Acc. Chem. Res.* **2016**, 49, 2605.
- [62] R. T. Perera, R. P. Johnson, M. A. Edwards, H. S. White, *J. Phys. Chem. C* **2015**, 119, 24299.
- [63] Z. Yanga, B. Cai, B. Zhou, T. Yao, W. Yu, S. Liu, W.-H. Zhang, C. Lia, *Nano Energy* **2015**, 15, 670.