Chapter 11

Organometal Halide Perovskites Thin Film and Their Impact on the Efficiency of Perovskite Solar Cells

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Additional information is available at the end of the chapter

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Abstract

The organometal halide perovskite solar cells (PSCs) have attracted attention and achieved efficiencies compared with traditional solar cells. There are several ways to develop perovskite solar cells like effect of moisture, degradation, and understanding the reason for instability of perovskite. In this chapter, we are specified how to make coating and film fabrication are affected by the existing methods. Improvement in the photovoltaic performance of PSCs can be achieved by enhanced processing technique. These techniques include the spin-coating PbI_2 solution controlling the substrate temperature and crystal quality of the morphology for perovskite films. There is no doubt that film coating indicates that the crystallization and morphology of perovskite films affect the absorption intensity and obviously influence the short-circuit current density. This study points out an enhancement of the stability of perovskite films and solar cells by reducing residual strains in perovskite films.

Keywords: perovskite solar cells, working mechanism, photovoltaic parameters, stability, low cost

1. Introduction

Metal halide perovskite solar cells (PSCs) have emerged as a kind of encouraging alternative to existing photovoltaic technologies with both solution processability and superior photovoltaic performances. Fundamental studies on perovskite materials [1], device designs [2, 3], fabrication processes [4–10], and materials engineering [11–16] have boosted the rapid development of PSCs. Consequently, a certified power conversion efficiency (PCE) of 22.1%

has been obtained after the past several years of vigorous work. However, despite the overwhelming achievements in terms of performance of PSCs, the long-term stability and current–voltage hysteresis still remain critical [4].

Perovskite solar cells, the most promising new technology in the academia and industry, have promised a highly competitive alternative to silicon solar cells and other commercial alternatives. Perovskite solar cells are high-performance photovoltaic devices which have the potential to enter in the market in the near future. Low processing costs and highly abundant raw materials may permit a short-energy payback time and low overall CO emissions. After an impressive increase in PCE from ~10% in 2012 to ~22.1% in early 2016, experts expect to discover further improvements in efficiency in the next several years [12]. Perovskite solar cell research is still in its infancy considering that the first work was only published in 2009 [1]. The commercialization of perovskite solar cell needs to address several fundamental issues in the near future: for example, control the growth of thin film and deposition, make scale and numerous process, achieve high stability and long lifetime, and low toxicity. To be competitive, cost will be a concern for manufacturing companies. Although the raw materials for making perovskite solar cells are inexpensive and abundant, recent analyses of cost-performance and commercialization requirements are not entirely positive [17]. To make perovskite solar cells competitive, several goals are needed to be achieved. For example, the levelized cost of electricity (LCOE) for residential use is 9.0 cents per kWh by 2020 and is expected to decline to 5.0 cents/kWh by 2030 [18]. This is a huge challenge for perovskite technology at present.

In this review, we summarize recently developed perovskite film deposition techniques and evaluate their suitability for industrial production of perovskite solar cells and modules. Our discussion of stability and device lifetime focuses mainly on the measurement standards and issues relative to commercialization. Thereafter, we present techniques that used to fabricate the perovskite solar cells such as one-step spin-coating and two-step deposition techniques, solvent-solvent extraction, vapor-assisted solution processes, dual-source vacuum deposition, hybrid deposition, hybrid chemical vapor deposition, sequential vapor deposition, and flash evaporation. The control of the morphology for perovskite thin films has been observed by many efforts.

2. The common architecture of PSC

Generally, PSC has three main types of device architectures: (i) mesoscopic structures using mesoporous semiconducting materials as electron-transporting layers (ETLs), i.e., TiO_2 [19], WO_3 [20], $SrTiO_3$ [21], ZnO [22], Zn_2SnO_4 [23], and SnO_2 [24]); (ii) meso-superstructures employing mesoporous insulators such as Al_2O_3 [25] and ZrO_2 [26] as scaffolds, while perovskite itself acts as ETL; and (iii) planar structures implementing ultrathin compact layer materials for both hole-blocking and electron-conducting purposes. Among these types, the planar PSC was motivated by the requests of more simple process and lower cost for future applications [27]. **Figure 1** reveals the evolution of device configuration as sequence from mesostructure to planar heterojunction. The categories related to the types of device architecture were discussed here in summary.

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2.1. The mesoporous scaffold

The best performance for PSCs have reported and reached a certified PCE of 22.1%, have depend on high temperature processing (450–550°C) and the mesoporous structure used TiO_2 as ETLs [29]. Moreover, in another work, a 16.2% efficiency was obtained from the combination of uniform and dense $MAPbI_3$ and $MAPbBr_3$ bilayer architecture consisting of perovskite-infiltrated mesoporous TiO_2 electrodes [30]. Similarly, the same group proceeded the $FAPbI_3$-$MAPbBr_3$ system with an architecture as follows: FTO/blocking TiO_2 (70 nm)/mesoporous TiO_2 and perovskite composite layer (200 nm)/perovskite upper layer (300 nm)/PTAA (50 nm)/Au (100 nm) with a PCE of 18.4% at maximum power point condition [31, 32].

A simple binder-free colloid Al_2O_3 nanoparticle meso-superstructured scaffold with annealing temperature of 150°C deposited over compact TiO_2 layer delivered PCEs of up to 12.3%. Furthermore, it has been revealed that a solid thin film of the perovskite absorber was formed on top of the scaffold thin porous Al_2O_3 films. This supported charge separation and transport of both carrier species with an internal quantum efficiency approaching 100% [33]. Mahmood et al. reported two-dimensional (2D) nanosheets with enhanced absorber infiltration as compared with 1D nanostructures as revealed in **Figure 2**. The author utilized WO_3 n-type semiconductor as a nanostructured porous ETL to obtain highly efficient perovskite solar cells with PCE of 11.2% [34].

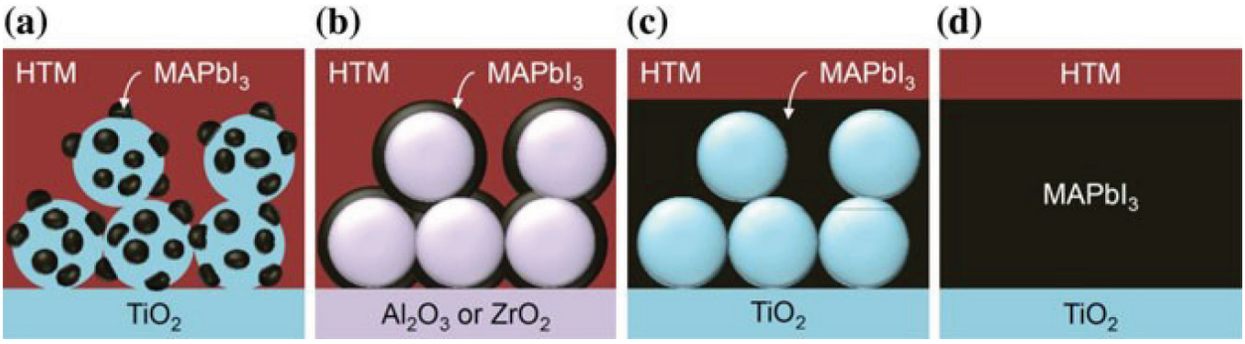

Figure 1. Development of device configuration in perovskite solar cells [28]. These figures reveal (a) a sensitization concept, (b) extremely thin layer of perovskite deposited on mesoporous scaffold layer, (c) perovskite infiltration into mesoporous film and (d) planar heterojunction structure.

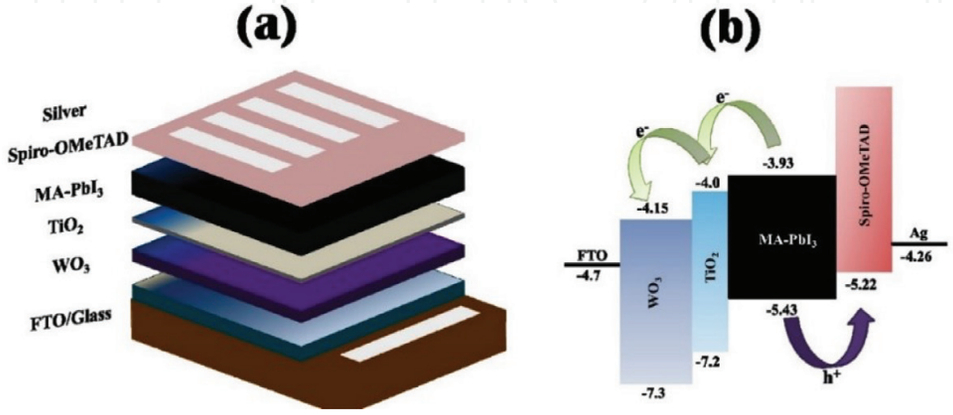

Figure 2. (a) Schematic cross section of WO_3 n-type semiconductor as a nanostructured porous ETL for perovskite solar cells and (b) energy band diagram [34].

2.2. The planar heterojunction

Planar PSCs have been demonstrated by Tan et al. with smooth and pinhole-free TiO_2-Cl as the ETL. The film also exhibited negligible parasitic absorption loss over the entire visible to near-infrared spectrum. Solar cells fabricated on TiO_2-Cl exhibit considerably better performance than those on TiO_2 for all PV parameters. Correspondingly, TiO_2-Cl resulted in a higher average PCE (19.8%) than the Cl-free TiO_2 (15.8%) [35, 36]. The best-performing small-area CsMAFA solar cell (0.049 cm^2) exhibited a high laboratory PCE of 21.4% without hysteresis in J-V sweeps. Similarly, large-area (1.1 cm^2) cells fabricated on TiO_2-Cl showed a PCE value >20% with negligible hysteresis. Zhou et al. manipulated carrier behavior with planar heterojunction perovskite solar cells. Yttrium-doped TiO_2 (Y-TiO_2) was fabricated at <150°C annealing temperature as the ETL to enhance electron extraction and transport over reduced work function ITO treated with polyethylenimine ethoxylated (PEIE) solution. These treatments produced a PCE of 19.3% [37, 38]. The use of CdSe nanoparticles (solution processed at 150°C) has been investigated to replace the widely used TiO_2 as the ETLs for the conventional planar heterojunction PSCs. Devices with CdSe nanoparticle ETLs were performed well, with the PCE of 11.7% [39]. A planar device with high PCE was applicable through Hagfeldt et al. and Jiang et al., using SnO_2 [24, 40–42].

By modifying the surface of a planar structure of the TiO_2 compact layer with C_{60}-SAM molecules (Wojciechowski et al.), a PCE of 15.7% has been obtained (**Figure 3**) [43]. Pablo Docampo et al. have demonstrated 10% PCEs for inverted planar PSCs with bilayer of $PC_{60}BM$ and compact TiO_x as ETL [44]. Further, hysteresis-less inverted planar hybrid solar cells with 18.1% PCE has been fabricated by Heo et al. Better PCE and stability were attributed to the electron extraction from $MAPbI_3$ into PCBM, the increased EQE value by the better charge injection/separation efficiency, and the improved FF by the increased diffusion coefficient (D_n) and charge carrier lifetime (τ_n). In addition, the air and humid stability was improved by the corrosive additive-free device architecture and hydrophobicity of the PCBM top layer [45].

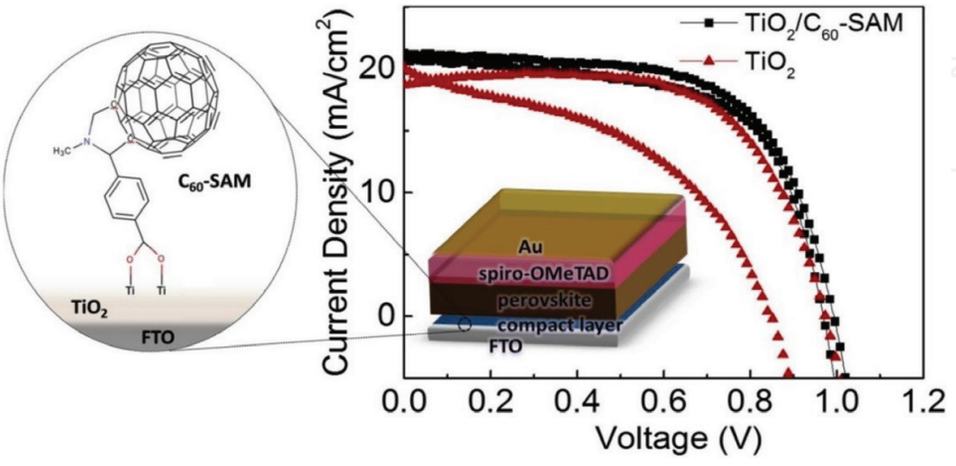

Figure 3. Planar structure of the TiO_2 compact layer with C_{60}-SAM molecules [43].

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3. Film formation of ETL

There is no doubt that the crystallinity, thickness, material film morphology, and purity have impact on the efficiency of solar cell performance. The film formation has been relied on deposition techniques such as one-step spin-coating [7, 46–50] and two-step deposition techniques [51, 52], solvent-solvent extraction [53], vapor-assisted solution processes [54–57], dual-source vacuum deposition [58–61], hybrid deposition [62, 63], hybrid chemical vapor deposition [62, 64–66], sequential vapor deposition [67, 68], and flash evaporation [69]. The control of the morphology for perovskite thin films has been observed by many efforts. These efforts include the optimization of the annealing time, temperature [70, 71], selection of the underlayer material and thickness [3, 72–75], and the use of alternative deposition methods such as two-step deposition and vacuum sublimation [4, 76, 77]. Herein, some of these methods have been discussed.

3.1. Vacuum thermal co-evaporation

In this method, the authors used vacuum thermal co-evaporation of organic halide and metal halide to resulting perovskite thin films with homogeneous morphology and improved thin-film coverage. These results achieved a high performance of 12–15% PCE [5, 78]. Despite the promising results, however, to date, only limited reports have utilized this vacuum sublimation technique to fabricate perovskite layers [5, 78]. The main reason could be due to the small molecular weight of organic halide and make the monitoring without control of the CH_3NH_3I deposition rate using quartz microbalance sensors [5, 78]. In another way, Zhu et al. reported how to develop this technique deposition to fabricate pinhole-free cesium-substituted perovskite films and enhance the surface coverage as shown in **Figure 4**. The same method used to promise tunable bandgap reduced trap-state density and longer carrier lifetime, with efficiency 20.13%, which is the highest fabrication for planar perovskite solar cells [79].

3.2. Layer-by-layer sequential vacuum sublimation

Chen et al. reported a novel method of perovskite thin-film deposition via a layer-by-layer sequential vacuum sublimation. This method has been easier than the previous technique. The very uniform perovskite thin films can achieve high coverage via incorporating the thin films of perovskite with a poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) hole-transporting layer (HTL) and thermally evaporated C60/bathophenanthroline (Bphen) electron-transporting layers (ETLs). The cells here attain efficiencies as high as 15.4% because the devices were free of high-temperature-prepared metal oxide layers [80].

3.3. Vapor deposition by dual source

The large-scale production in optoelectronic applications has been achieved by vapor deposition techniques because this technique is widely used in semiconductor industry. The feasibility of organometal halide perovskite materials via vapor deposition techniques

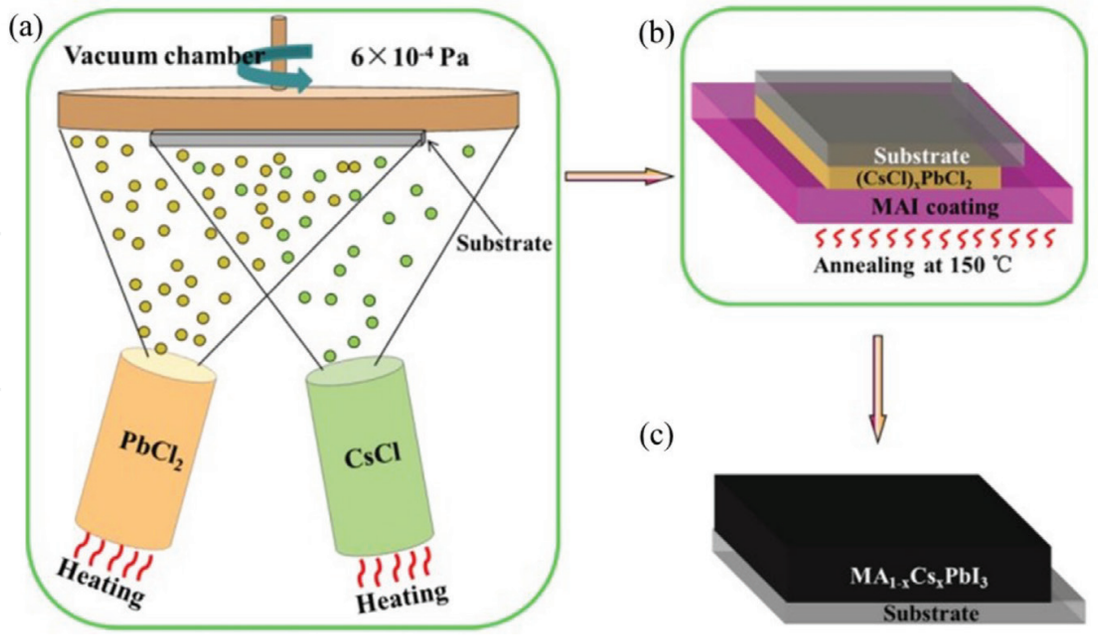

Figure 4. (a) Illustration of the vacuum co-evaporation, (b) deposition of the Cs-substituted $MA_{1-x}Cs_xPbI_3$ perovskite thin film and (c) final perovskite thin film [79].

has advantages like the possibility to fabricate films with high purity; these techniques are more proper to prepare multilayered structures of thin films, and suitable optimization of perovskite films also can be deposited by vapor deposition [5, 81]. Liu et al. [5] reported preparation of $CH_3NH_3PbI_{3-x}Cl_x$ by dual-source vapor deposition technique in the presence of $PbCl_2$ and CH_3NH_3I. This method leads to high-efficiency photovoltaic devices of 15.4%. Malinkiewicz et al. used the same technique to deposited $CH_3NH_3PbI_3$ in the presence of PbI_2 and CH_3NH_3I and give uniform film formation with root-mean-square roughness of 5 nm measured by AFM [81]. In addition, the films showed uniform grainy structures with an average grain size of 150 nm [82]. Schematic illustration of the dual-source vacuum deposition process is shown in **Figure 5** [59].

3.4. Spin coating

Spin coating is widely used to fabricate a small area from thin films in lab scale. Spin coating used a small amount of solution, which was then dropped on the substrate as shown in **Figure 6a**. Then, the substrate has been covered by a layer of solution and spun to accelerate evaporation of the solvent [83]. This technique controls the thickness of the film by the concentration of the solution and speed [83]. In general, with regular spin coating, a one-step process with PbI_2/MAI or $PbCl_2$/MAI with gamma-butyrolactone (GBL), dimethylformamide (DMF), or dimethyl sulfoxide (DMSO) as solvents prompts poor film quality [71, 84]. Despite the fact that all preparing conditions have been considered, spin-coated perovskite film quality is regularly poor, with a high thickness of pinholes and little grain sizes. These pinholes cause shunt that debase the efficiency. With added substances designing the crystallization

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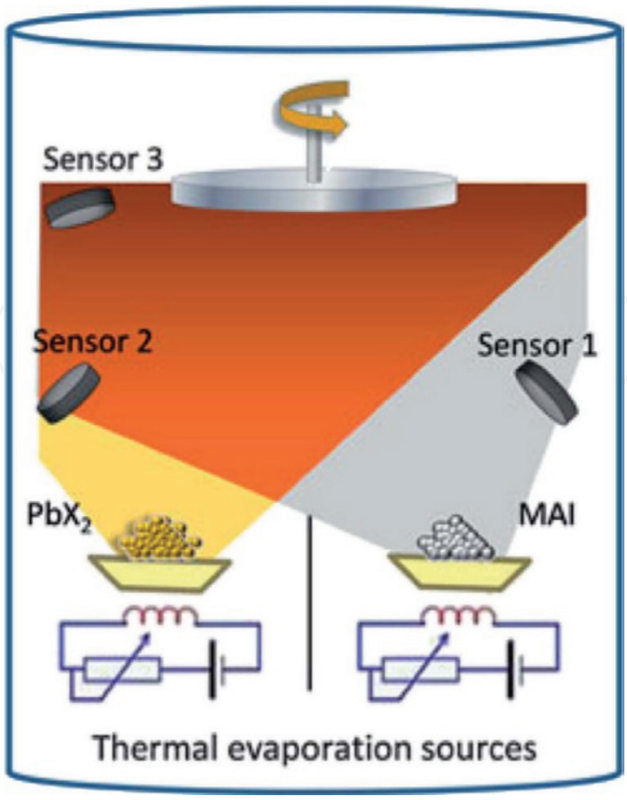

Figure 5. Description of the dual-source vacuum deposition instrument (reproduced with permission from Ref. [59]).

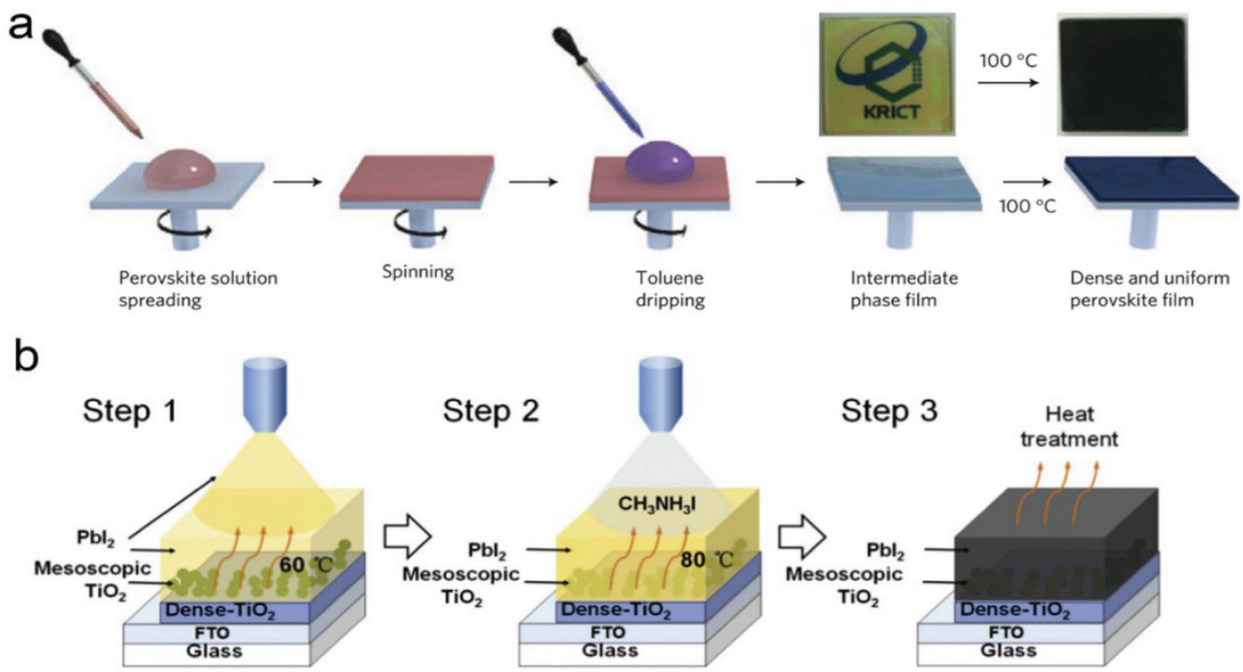

Figure 6. Different techniques used for large-area perovskite film deposition: (a) spin-coating technique and (b) spray-coating technique (reproduced with permission [6, 98]).

of perovskite could be finely tuned, and perovskite films with altogether enhanced quality can be set up for superior power conversion [85, 86]. For instance, by utilizing lead acetic acid as lead source, the crystallization of perovskite is significantly speedier. The free pinhole perovskite films were shown by a basic one-step coating process [87].

Concerning the two-step process, made to create good morphology perovskite films, convolutes control over the change rate of PbI_2 to perovskite [4]. In the recent date, it has been demonstrated that the order of PbI_2-DMSO-MAI essentially improves the film morphology and quality utilizing a propelled hostile to dissolved designing strategy [6, 88, 89]. Furthermore, this hot-throwing procedure could be exchanged to a considerably less difficult plunge-covering process for large-area film deposition. There is no doubt that the high performance and scale of large area for PSCs are closely related to perovskite film quality. A 1-cm^2 PSC was fabricated for the first time with a modified interface layer and certified efficiency of 15.6% [90]. Then, enhancing the gradient of heterojunction structure for charge separation/transport, its performance increased to 18.21% [91]. Moreover, a vacuum, flash-assisted process has been produced by a solar cell with a 1-cm^2 area [92]. This technique showed a maximum efficiency of 20.5% and a certified efficiency of 19.6% [93].

3.5. Spray coating

Spray coating has been broadly utilized to deposit perovskite films and compact TiO_2 films and is perfect with large-scale, high-throughput manufacture (**Figure 6b**). The first thinking about how to get perovskite films via spray coating came from polymer solar cell fabrication. An ultrasonic spray-coating technique has been discovered in ambient conditions. In this method a system from DMF or DMSO and perovskite materials was investigated with deposition parameter to achieve higher coverage of perovskite films. The parameters which are related to spray coating require to form high-coverage perovskite film such as drying time, substrate temperature, solvent volatility, and post-annealing conditions. With PCE of 11% and an active area about 0.025 cm^2, the potential of spray coating in fabricating perovskite solar cells has been indicated [94]. A similar work was performed in TiO_2 and achieved PCE of 13% with 0.065 cm^2 active area on a glass/ITO substrate. In low-temperature PET/ITO substrate in the presence of TiO_2, an efficiency of 8.1% was attained on a flexible device, which is comparable with roll-to-roll processing [95]. This spray-coating process is suitable for various perovskite precursor solutions; for example, spray-coating deposition of large bandgap $CsPbIBr_2$ thin films has a potential for tandem structure devices [96]. Other mixed cations and halide perovskites, $FA_{1-x}Cs_xPbI_3$ mixed cation films, were prepared with a spray-assisted solution process [97]. Solar cell devices based on this mixed cation film showed enhanced stability and performance compared with those based on the other. Efficiency increased from 11.3 to 14.2% for the mixed cations.

3.6. Screen printing

Screen printing is a technique used to fabricate PSCs that could be easily fabricated with a printing process. The layer-by-layer printing process starts with screen printing of TiO_2, followed by printing of ZrO_2 and carbon electrodes. Then, perovskite solution is dropped onto the porous carbon electrode so that it infiltrates into the mesoporous TiO_2 and ZrO_2. Herein,

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ZrO_2 functions as a porous insulating layer to prevent direct contact between the carbon electrode and the TiO_2/FTO substrate. Although it is easy to fabricate solar cells with this printing technique, infiltration of perovskite precursor solution remains a challenge and is the main reason for lower efficiency compared to those of devices fabricated by other means. The most intriguing properties of this carbon-coated, printed, mesoscopic device are the high stability and outstanding outdoor performance. A certified PCE of 12.8% and stable performance over >1000 h in ambient air under full sunlight has been recorded for a device with an active area of 0.28 cm^2 [26, 99]. **Figure 7** shows noncontact inkjet printing offering rapid and digital deposition combined with excellent control over the layer formation for printed perovskite solar cells. Mathies et al. [100] reported that inkjet printing is used to deposit triple cation perovskite layers with 10% cesium in a mixed formamidinium/methylammonium lead iodide/bromide composite for solar cells with high temperature and moisture stability. A reliable process control over a wide range of perovskite layer thickness from 175 to 780 nm and corresponding grain sizes is achieved by adjusting the drop spacing of the inkjet printer cartridge. A continuous power output at constant voltage, resulting in a power conversion efficiency of 12.9%, is demonstrated, representing a major improvement from previously reported inkjet-printed methylammonium lead triiodide perovskite solar cells [100]. Compared with solution processes, dry deposition processes may be more environmentally friendly, as they do not require toxic solvents (DMSO, GBL, DMF, chloroform, chlorobenzene, isopropanol, toluene, diethyl ether, etc.), and they are compatible with high-quality, large-area perovskite film deposition, such as vacuum deposition and chemical vapor deposition.

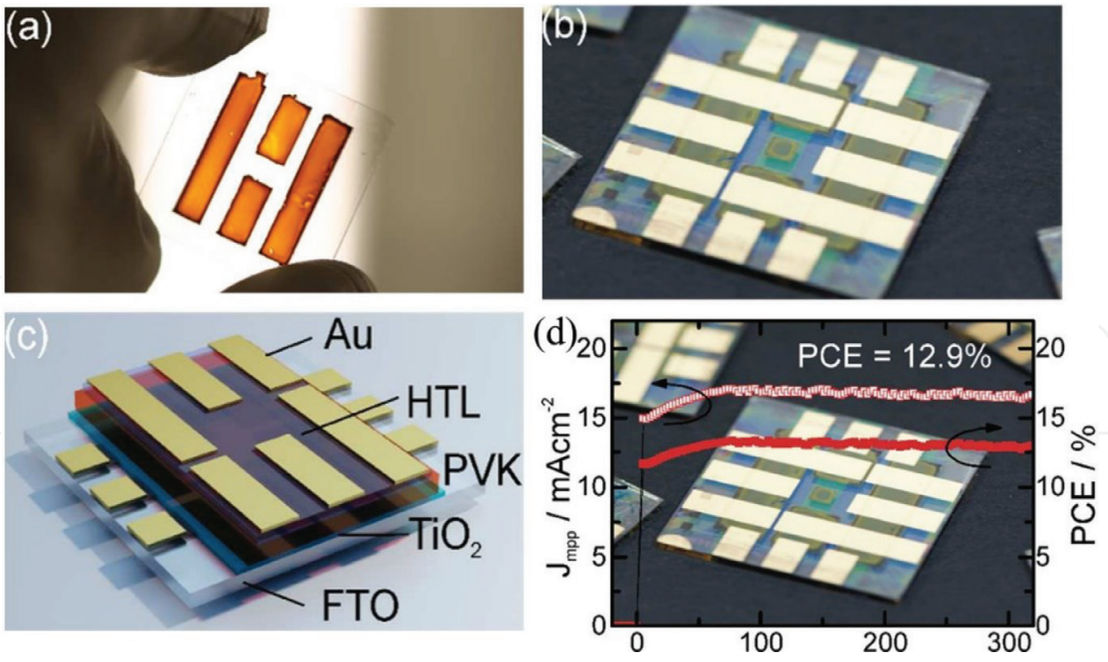

Figure 7. (a) 520 nm-thick inkjet-printed perovskite layer on FTO/TiO_2-coated glass substrate. (b) Photograph of inkjet-printed perovskite solar cells. The substrate contains eight cells with each 3×3 mm^2 active area. (c) Schematic diagram of the solar cell stack, denoting with the different layers: glass/FTO/TiO_2/triple cation perovskite (PVK)/Spiro-MeOTAD (HTL)/Au [100]. (d) Real solar cell achieved 12% with the configuration: Glass/FTO/TiO_2/triple cation perovskite (PVK)/Spiro-MeOTAD (HTL)/Au.

4. Summary and future outlook

The effectivity of photon capture in PSCs has resulted in tangible action and contributed to scientific community [101]. These achievements have an economic impact for future endeavor. Therefore, the innovation in PSC field required a large amount of effort and attention to be reliable and highly efficient at converting sunlight to electricity. Furthermore, the improvement of device engineering methods is urgent. In particular, investigation of photophysical mechanism of the materials also plays an important role. The continuous investigation on current density and voltage characteristics of PSCs would provide a good understanding point for the semiconducting behavior [102]. The improvement in PSC efficiency relies on deposition techniques and material composition [103]. The solution processed in PSCs is more important [104]. We are noticed that the one-step spin coating is broadly the used method because of its simplicity and low cost. The films synthesized by this method have a poor morphology and incomplete coverage, for instance, in the case of planar architecture [84, 85, 105]. On the other hand, in the two-step coating, a layer of lead halide was deposited by spin coating then followed by immerging in organic salt solution and the perovskite films formed by a chemical reaction [51, 52]. The high reaction rates of perovskite materials are important to optimize the coating conditions with sufficient reproducibility. To record high efficiencies by solution processing, it is revealed that the reaction kinetics are required to control and maintain consistent device to minimize batch-to-batch variations. The different vapor-based methods to deposit perovskite films are also discussed, which in many cases show properties different from their counterparts prepared by solution-based methods.

Conflict of interest

The authors declare no conflict of interest.

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References

[1] Kojima A, Teshima K, Shirai Y, Miyasaka T. Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. Journal of the American Chemical Society. 2009;**131**(17):6050-6051. DOI: 10.1021/ja809598r

[2] Lee MM, Teuscher J, Miyasaka T, Murakami TN, Snaith HJ. Efficient hybrid solar cells based on meso-superstructured organometal halide perovskites. Science. 2012;**338**(6107): 643-647

[3] Kim H-S, Lee C-R, Im J-H, et al. Lead iodide perovskite sensitized all-solid-state submicron thin film mesoscopic solar cell with efficiency exceeding 9%. Scientific Reports. 2012;**2**:591

[4] Burschka J, Pellet N, Moon S-J, et al. Sequential deposition as a route to high-performance perovskite-sensitized solar cells. Nature. 2013;**499**(7458):316

[5] Liu M, Johnston MB, Snaith HJ. Efficient planar heterojunction perovskite solar cells by vapour deposition. Nature. 2013;**501**(7467):395

[6] Jeon NJ, Noh JH, Kim YC, Yang WS, Ryu S, Seok SI. Solvent engineering for high-performance inorganic–organic hybrid perovskite solar cells. Nature Materials. 2014;**13**(9):897

[7] Elseman AM, Rashad MM, Hassan AM. Easily attainable, efficient solar cell with mass yield of nanorod single-crystalline organo-metal halide perovskite based on a ball milling technique. ACS Sustainable Chemistry & Engineering. 2016;**4**(9):4875-4886

[8] Elseman AM, Shalan AE, Sajid S, Rashad MM, Hassan AM, Li M. Copper substituted lead perovskites materials constructed with different halides for working $(CH_3NH_3)_2CuX_4$ based perovskite solar cells from experimental and theoretical view. ACS Applied Materials & Interfaces. 2018;**10**(14):11699-11707. DOI: 10.1021/acsami.8b00495

[9] Sajid AME, Ji J, Dou S, Huang H, Cui P, Wei D, Li M. Novel hole transport layer of nickel oxide composite with carbon for high-performance perovskite solar cells. Chinese Physics B. 2018;**27**(1):17305. DOI: 10.1088/1674-1056/27/1/017305

[10] Shalan AE, Barhoum A, Elseman AM, Rashad MM, Lira-Cantú M. Nanofibers as promising materials for new generations of solar cells. In: Barhoum A, Bechelany M, Makhlouf A, editors. Handbook of Nanofibers. Cham: Springer International Publishing; 2018. pp. 1-33

[11] Jeon NJ, Noh JH, Yang WS, et al. Compositional engineering of perovskite materials for high-performance solar cells. Nature. 2015;**517**(7535):476

[12] Yang WS, Noh JH, Jeon NJ, et al. High-performance photovoltaic perovskite layers fabricated through intramolecular exchange. Science. 2015;**348**(6240):1234-1237

[13] Yuan XZ, Chao W, Shi H. Determination of slip length in couette flow based on an analytical simulation incorporating surface interaction. 2017;**34**(3):034701. DOI: 10.1088/0256-307X/34/3/034701:

[14] Yao J, Wei Q, Ma QY, Wu DJ. Dielectric loaded surface plasmon polariton properties of the Al–Al nanostructure. Chinese Physics B. 2017;**26**(5):057302

[15] Zeng HD, Zhu ZY, Zhang JD, Cheng XL. Diffusion and thermite reaction process of film-honeycomb Al/NiO nanothermite: Molecular dynamics simulations using ReaxFF reactive force field. Chinese Physics B. 2017;**26**(5):056101

[16] Liu P, Yang BC, Liu G, Wu RS, Zhang CJ, Wan F, Li SG, Yang JL, Gao YL, Zhou CH. Improving power conversion efficiency of perovskite solar cells by cooperative LSPR of gold-silver dual nanoparticles. Chinese Physics B. 2017;**26**(5):058401

[17] Molang C, Yongzhen W, Han C, Xudong Y, Yinghuai Q, Liyuan H. Cost-performance analysis of perovskite solar modules. Advanced Science. 2017;**4**(1):1600269. DOI: 10.1002/advs.201600269

[18] Chu S, Cui Y, Liu N. The path towards sustainable energy. Nature Materials. 2016;**16**:16. DOI: 10.1038/nmat4834

[19] Im J-H, Jang I-H, Pellet N, Grätzel M, Park N-G. Growth of $CH_3NH_3PbI_3$ cuboids with controlled size for high-efficiency perovskite solar cells. Nature Nanotechnology. 2014;**9**(11):927-932. DOI: 10.1038/nnano.2014.181

[20] Wang F, Di Valentin C, Pacchioni G. Rational band gap engineering of WO_3 photocatalyst for visible light water splitting. ChemCatChem. 2012;**4**(4):476-478. DOI: 10.1002/cctc.201100446

[21] Okamoto Y, Fukui R, Fukazawa M, Suzuki Y. $SrTiO_3/TiO_2$ composite electron transport layer for perovskite solar cells. Materials Letters. 2017;**187**(Supplement C):111-113. DOI: 10.1016/j.matlet.2016.10.090

[22] Son D-Y, Im J-H, Kim H-S, Park N-G. 11% efficient perovskite solar cell based on ZnO nanorods: An effective charge collection system. The Journal of Physical Chemistry C. 2014;**118**(30):16567-16573. DOI: 10.1021/jp412407j

[23] Oh LS, Kim DH, Lee JA, et al. Zn_2SnO_4-based photoelectrodes for organolead halide perovskite solar cells. The Journal of Physical Chemistry C. 2014;**118**(40):22991-22994. DOI: 10.1021/jp509183k

[24] Correa Baena JP, Steier L, Tress W, et al. Highly efficient planar perovskite solar cells through band alignment engineering. Energy & Environmental Science. 2015;**8**(10):2928-2934. DOI: 10.1039/c5ee02608c

[25] Hu YH. Novel meso-superstructured solar cells with a high efficiency exceeding 12%. Advanced Materials. 2014;**26**(13):2102-2104. DOI: 10.1002/adma.201304732

[26] Mei A, Li X, Liu L, et al. A hole-conductor-free, fully printable mesoscopic perovskite solar cell with high stability. Science. 2014;**345**(6194):295-298. DOI: 10.1126/science.1254763

[27] Chen B-X, Rao H-S, Li W-G, et al. Achieving high-performance planar perovskite solar cell with Nb-doped TiO_2 compact layer by enhanced electron injection and efficient charge extraction. Journal of Materials Chemistry A. 2016;**4**(15):5647-5653. DOI: 10.1039/C6TA00989A

[28] Park NG, Miyasaka T, Grätzel M. Organic-inorganic halide perovskite photovoltaics. Cham, Switzerland: Springer; 2016

[29] Tan H, Jain A, Voznyy O, et al. Efficient and stable solution-processed planar perovskite solar cells via contact passivation. Science. 2017;**355**(6326):722-726. DOI: 10.1126/science.aai9081

[30] Jeon NJ, Noh JH, Kim YC, Yang WS, Ryu S, Seok SI. Solvent engineering for high-performance inorganic–organic hybrid perovskite solar cells. Nature Materials. 2014;**13**(9):897-903. DOI: 10.1038/nmat4014

[31] Jeon NJ, Noh JH, Yang WS, et al. Compositional engineering of perovskite materials for high-performance solar cells. Nature. 2015;**517**(7535):476-480. DOI: 10.1038/nature14133

[32] Saliba M, Matsui T, Domanski K, et al. Incorporation of rubidium cations into perovskite solar cells improves photovoltaic performance. Science. 2016;**354**(6309):206-209. DOI: 10.1126/science.aah5557

[33] Ball JM, Lee MM, Hey A, Snaith HJ. Low-temperature processed meso-superstructured to thin-film perovskite solar cells. Energy and Environmental Scinece. 2013;**6**:1739-1743

[34] Mahmood K, Swain BS, Kirmani AR, Amassian A. Highly efficient perovskite solar cells based on a nanostructured WO_3–TiO_2core–shell electron transporting material. Journal of Materials Chemistry A. 2015;**3**(17):9051-9057. DOI: 10.1039/c4ta04883k

[35] Saliba M, Matsui T, Seo J-Y, et al. Cesium-containing triple cation perovskite solar cells: improved stability, reproducibility and high efficiency. Energy & Environmental Science. 2016;**9**(6):1989-1997. DOI: 10.1039/C5EE03874J

[36] Li Z, Yang M, Park J-S, Wei S-H, Berry JJ, Zhu K. Stabilizing perovskite structures by tuning tolerance factor: Formation of formamidinium and cesium lead iodide solid-state alloys. Chemistry of Materials. 2016;**28**(1):284-292. DOI: 10.1021/acs.chemmater.5b04107

[37] Zhou Y, Fuentes-Hernandez C, Shim J, et al. A universal method to produce low–work function electrodes for organic electronics. Science. 2012;**336**(6079):327-332. DOI: 10.1126/science.1218829

[38] Zhou H, Chen Q, Li G, et al. Interface engineering of highly efficient perovskite solar cells. Science. 2014;**345**(6196):542-546

[39] Wang L, Fu W, Gu Z, et al. Low temperature solution processed planar heterojunction perovskite solar cells with a CdSe nanocrystal as an electron transport/extraction layer. Journal of Materials Chemistry C. 2014;**2**(43):9087-9090. DOI: 10.1039/C4TC01875C

[40] Jiang Q, Zhang L, Wang H, et al. Enhanced electron extraction using SnO_2 for high-efficiency planar-structure $HC(NH_2)_2PbI_3$-based perovskite solar cells. Nature Energy. 2016;**2**:16177. DOI: 10.1038/nenergy.2016.177

[41] Ke W, Fang G, Liu Q, et al. Low-temperature solution-processed tin oxide as an alternative electron transporting layer for efficient perovskite solar cells. Journal of the American Chemical Society. 2015;**137**(21):6730-6733. DOI: 10.1021/jacs.5b01994

[42] Anaraki EH, Kermanpur A, Steier L, et al. Highly efficient and stable planar perovskite solar cells by solution-processed tin oxide. Energy & Environmental Science. 2016;**9**(10):3128-3134. DOI: 10.1039/C6EE02390H

[43] Wojciechowski K, Stranks SD, Abate A, et al. Heterojunction modification for highly efficient organic–inorganic perovskite solar cells. ACS Nano. 2014;**8**(12):12701-12709. DOI: 10.1021/nn505723h

[44] Docampo P, Ball JM, Darwich M, Eperon GE, Snaith HJ. Efficient organometal trihalide perovskite planar-heterojunction solar cells on flexible polymer substrates. Nature Communications. 2013;**4**:2761. DOI: 10.1038/ncomms3761

[45] Heo JH, Han HJ, Kim D, Ahn TK, Im SH. Hysteresis-less inverted $CH_3NH_3PbI_3$ planar perovskite hybrid solar cells with 18.1% power conversion efficiency. Energy & Environmental Science. 2015;**8**(5):1602-1608. DOI: 10.1039/C5EE00120J

[46] Wojciechowski K, Saliba M, Leijtens T, Abate A, Snaith HJ. Sub-150 C processed meso-superstructured perovskite solar cells with enhanced efficiency. Energy & Environmental Science. 2014;**7**(3):1142-1147

[47] Wang JT-W, Ball JM, Barea EM, et al. Low-temperature processed electron collection layers of graphene/TiO_2 nanocomposites in thin film perovskite solar cells. Nano Letters. 2013;**14**(2):724-730

[48] Edri E, Kirmayer S, Cahen D, Hodes G. High open-circuit voltage solar cells based on organic–inorganic lead bromide perovskite. The Journal of Physical Chemistry Letters. 2013;**4**(6):897-902

[49] Rashad MM, Elseman AM, Hassan AM. Facile synthesis, characterization and structural evolution of nanorods single-crystalline $(C_4H_9NH_3)_2PbI_2X_2$ mixed halide organometal perovskite for solar cell application. Optik-International Journal for Light and Electron Optics. 2016;**127**(20):9775-9787

[50] Elseman A, Shalan A, Rashad M, Hassan A. Experimental and simulation study for impact of different halides on the performance of planar perovskite solar cells. Materials Science in Semiconductor Processing. 2017;**66**:176-185

[51] Liang K, Mitzi DB, Prikas MT. Synthesis and characterization of organic-inorganic perovskite thin films prepared using a versatile two-step dipping technique. Chemistry of Materials. 1998;**10**(1):403-411

[52] Mitzi DB. Thin-film deposition of organic-inorganic hybrid materials. Chemistry of Materials. 2001;**13**(10):3283-3298

[53] Zhou Y, Yang M, Wu W, Vasiliev AL, Zhu K, Padture NP. Room-temperature crystallization of hybrid-perovskite thin films via solvent–solvent extraction for high-performance solar cells. Journal of Materials Chemistry A. 2015;**3**(15):8178-8184

[54] Du T, Wang N, Chen H, Lin H, He H. Comparative study of vapor-and solution-crystallized perovskite for planar heterojunction solar cells. ACS Applied Materials & Interfaces. 2015;**7**(5):3382-3388

[55] Sheng R, Ho-Baillie A, Huang S, et al. Methylammonium lead bromide perovskite-based solar cells by vapor-assisted deposition. The Journal of Physical Chemistry C. 2015; **119**(7):3545-3549

[56] Zhou H, Chen Q, Yang Y. Vapor-assisted solution process for perovskite materials and solar cells. MRS Bulletin. 2015;**40**(8):667-673

[57] Chen Q, Zhou H, Song T-B, et al. Controllable self-induced passivation of hybrid lead iodide perovskites toward high performance solar cells. Nano Letters. 2014;**14**(7): 4158-4163

[58] Ono LK, Leyden MR, Wang S, Qi Y. Organometal halide perovskite thin films and solar cells by vapor deposition. Journal of Materials Chemistry A. 2016;**4**(18):6693-6713

[59] Sessolo M, Momblona C, Gil-Escrig L, Bolink HJ. Photovoltaic devices employing vacuum-deposited perovskite layers. MRS Bulletin. 2015;**40**(8):660-666

[60] Kim B-S, Kim T-M, Choi M-S, Shim H-S, Kim J-J. Fully vacuum–processed perovskite solar cells with high open circuit voltage using MoO_3/NPB as hole extraction layers. Organic Electronics. 2015;**17**:102-106

[61] Malinkiewicz O, Roldán-Carmona C, Soriano A, et al. Metal-oxide-free methylammonium lead iodide perovskite-based solar cells: The influence of organic charge transport layers. Advanced Energy Materials. 2014;**4**(15):1400345

[62] Teuscher J, Ulianov A, Müntener O, Grätzel M, Tétreault N. Control and study of the stoichiometry in evaporated perovskite solar cells. ChemSusChem. 2015;**8**(22):3847-3852

[63] Ono LK, Wang S, Kato Y, Raga SR, Qi Y. Fabrication of semi-transparent perovskite films with centimeter-scale superior uniformity by the hybrid deposition method. Energy & Environmental Science. 2014;**7**(12):3989-3993

[64] Luo P, Liu Z, Xia W, et al. Chlorine-conducted defect repairment and seed crystal-mediated vapor growth process for controllable preparation of efficient and stable perovskite solar cells. Journal of Materials Chemistry A. 2015;**3**(45):22949-22959

[65] Luo P, Liu Z, Xia W, Yuan C, Cheng J, Lu Y. A simple in situ tubular chemical vapor deposition processing of large-scale efficient perovskite solar cells and the research on their novel roll-over phenomenon in J–V curves. Journal of Materials Chemistry A. 2015; **3**(23):12443-12451

[66] Leyden MR, Ono LK, Raga SR, Kato Y, Wang S, Qi Y. High performance perovskite solar cells by hybrid chemical vapor deposition. Journal of Materials Chemistry A. 2014; **2**(44):18742-18745

[67] Ng A, Ren Z, Shen Q, et al. Efficiency enhancement by defect engineering in perovskite photovoltaic cells prepared using evaporated PbI_2/CH_3NH_3I multilayers. Journal of Materials Chemistry A. 2015;**3**(17):9223-9231

[68] Yang D, Yang Z, Qin W, Zhang Y, Liu SF, Li C. Alternating precursor layer deposition for highly stable perovskite films towards efficient solar cells using vacuum deposition. Journal of Materials Chemistry A. 2015;**3**(18):9401-9405

[69] Longo G, Gil-Escrig L, Degen MJ, Sessolo M, Bolink HJ. Perovskite solar cells prepared by flash evaporation. Chemical Communications. 2015;**51**(34):7376-7378

[70] Jeng JY, Chiang YF, Lee MH, et al. $CH_3NH_3PbI_3$ perovskite/fullerene planar-heterojunction hybrid solar cells. Advanced Materials. 2013;**25**(27):3727-3732

[71] Eperon GE, Burlakov VM, Docampo P, Goriely A, Snaith HJ. Morphological control for high performance, solution-processed planar heterojunction perovskite solar cells. Advanced Functional Materials. 2014;**24**(1):151-157

[72] Bi D, Moon S-J, Häggman L, et al. Using a two-step deposition technique to prepare perovskite ($CH_3NH_3PbI_3$) for thin film solar cells based on ZrO_2 and TiO_2 mesostructures. RSC Advances. 2013;**3**(41):18762-18766

[73] Jeng JY, Chen KC, Chiang TY, et al. Nickel oxide electrode interlayer in $CH_3NH_3PbI_3$ perovskite/PCBM planar-heterojunction hybrid solar cells. Advanced Materials. 2014; **26**(24):4107-4113

[74] Ball JM, Lee MM, Hey A, Snaith HJ. Low-temperature processed meso-superstructured to thin-film perovskite solar cells. Energy & Environmental Science. 2013;**6**(6):1739-1743

[75] Yella A, Heiniger L-P, Gao P, Nazeeruddin MK, Grätzel M. Nanocrystalline rutile electron extraction layer enables low-temperature solution processed perovskite photovoltaics with 13.7% efficiency. Nano Letters. 2014;**14**(5):2591-2596

[76] Ma Y, Zheng L, Chung Y-H, et al. A highly efficient mesoscopic solar cell based on $CH_3NH_3PbI_{3-x}Cl_x$ fabricated via sequential solution deposition. Chemical Communications. 2014;**50**(83):12458-12461

[77] Chen Q, Zhou H, Hong Z, et al. Planar heterojunction perovskite solar cells via vapor-assisted solution process. Journal of the American Chemical Society. 2013;**136**(2):622-625

[78] Malinkiewicz O, Yella A, Lee YH, et al. Perovskite solar cells employing organic charge-transport layers. Nature Photonics. 2014;**8**(2):128-132

[79] Zhu X, Yang D, Yang R, et al. Superior stability for perovskite solar cells with 20% efficiency using vacuum co-evaporation. Nanoscale. 2017;**9**(34):12316-12323. DOI: 10.1039/C7NR04501H

[80] Chen CW, Kang HW, Hsiao SY, Yang PF, Chiang KM, Lin HW. Efficient and uniform planar-type perovskite solar cells by simple sequential vacuum deposition. Advanced Materials. 2014;**26**(38):6647-6652

[81] Malinkiewicz O, Yella A, Lee YH, et al. Perovskite solar cells employing organic charge-transport layers. Nature Photonics. 2014;**8**(2):128

[82] Momblona C, Malinkiewicz O, Roldán-Carmona C, et al. Efficient methylammonium lead iodide perovskite solar cells with active layers from 300 to 900 nm. APL Materials. 2014;**2**(8):081504

[83] Heo JH, Song DH, Im SH. Planar $CH_3NH_3PbBr_3$ hybrid solar cells with 10.4% power conversion efficiency, fabricated by controlled crystallization in the spin-coating process. Advanced Materials. 2014;**26**(48):8179-8183

[84] Dualeh A, Tétreault N, Moehl T, Gao P, Nazeeruddin MK, Grätzel M. Effect of annealing temperature on film morphology of organic–inorganic hybrid pervoskite solid-state solar cells. Advanced Functional Materials. 2014;**24**(21):3250-3258

[85] Liang PW, Liao CY, Chueh CC, et al. Additive enhanced crystallization of solution-processed perovskite for highly efficient planar-heterojunction solar cells. Advanced Materials. 2014;**26**(22):3748-3754

[86] Moore DT, Sai H, Tan KW, et al. Crystallization kinetics of organic–inorganic trihalide perovskites and the role of the lead anion in crystal growth. Journal of the American Chemical Society. 2015;**137**(6):2350-2358

[87] Zhang W, Saliba M, Moore DT, et al. Ultrasmooth organic–inorganic perovskite thin-film formation and crystallization for efficient planar heterojunction solar cells. Nature Communications. 2015;**6**:6142

[88] Ahn N, Son D-Y, Jang I-H, Kang SM, Choi M, Park N-G. Highly reproducible perovskite solar cells with average efficiency of 18.3% and best efficiency of 19.7% fabricated via Lewis base adduct of lead (II) iodide. Journal of the American Chemical Society. 2015; **137**(27):8696-8699

[89] Xiao M, Huang F, Huang W, et al. A fast deposition-crystallization procedure for highly efficient lead iodide perovskite thin-film solar cells. Angewandte Chemie. 2014;**126**(37): 10056-10061

[90] Chen W, Wu Y, Yue Y, et al. Efficient and stable large-area perovskite solar cells with inorganic charge extraction layers. Science. 2015;**350**(6263):944-948

[91] Wu Y, Yang X, Chen W, et al. Perovskite solar cells with 18.21% efficiency and area over 1 cm^2 fabricated by heterojunction engineering. Nature Energy. 2016;**1**(11):16148

[92] Li X, Bi D, Yi C, et al. A vacuum flash–assisted solution process for high-efficiency large-area perovskite solar cells. Science. 2016;aaf8060

[93] Seo J, Park S, Kim YC, et al. Benefits of very thin PCBM and LiF layers for solution-processed p–i–n perovskite solar cells. Energy & Environmental Science. 2014;**7**(8):2642-2646

[94] Barrows AT, Pearson AJ, Kwak CK, Dunbar AD, Buckley AR, Lidzey DG. Efficient planar heterojunction mixed-halide perovskite solar cells deposited via spray-deposition. Energy & Environmental Science. 2014;**7**(9):2944-2950

[95] Das S, Yang B, Gu G, et al. High-performance flexible perovskite solar cells by using a combination of ultrasonic spray-coating and low thermal budget photonic curing. ACS Photonics. 2015;**2**(6):680-686

[96] Lau CFJ, Deng X, Ma Q, et al. $CsPbIBr_2$ perovskite solar cell by spray-assisted deposition. ACS Energy Letters. 2016;**1**(3):573-577

[97] Xia X, Wu W, Li H, et al. Spray reaction prepared $FA_{1-x}Cs_xPbI_3$ solid solution as a light harvester for perovskite solar cells with improved humidity stability. RSC Advances. 2016;**6**(18):14792-14798

[98] Huang H, Shi J, Zhu L, Li D, Luo Y, Meng Q. Two-step ultrasonic spray deposition of $CH_3NH_3PbI_3$ for efficient and large-area perovskite solar cell. Nano Energy. 2016; **27**:352-358

[99] Li X, Tschumi M, Han H, et al. Outdoor performance and stability under elevated temperatures and long-term light soaking of triple-layer mesoporous perovskite photovoltaics. Energy Technology. 2015;**3**(6):551-555

[100] Mathies F, Eggers H, Richards BS, Hernandez-Sosa G, Lemmer U, Paetzold UW. Inkjet-printed triple cation perovskite solar cells. ACS Applied Energy Materials. 2018;**1**(5): 1834-1839. DOI: 10.1021/acsaem.8b00222

[101] Park N-G. Perovskite solar cells: an emerging photovoltaic technology. Materials Today. 2015;**18**(2):65-72. DOI: 10.1016/j.mattod.2014.07.007

[102] Meloni S, Moehl T, Tress W, et al. Ionic polarization-induced current-voltage hysteresis in $CH_3NH_3PbX_3$ perovskite solar cells. Nature Communications. Feb 8 2016;**7**:10334. DOI: 10.1038/ncomms10334

[103] Back H, Kim J, Kim G, et al. Interfacial modification of hole transport layers for efficient large-area perovskite solar cell achieved via blade-coating. Solar Energy Materials and Solar Cells. 2016;**144**(Supplement C):309-315. DOI: 10.1016/j.solmat.2015.09.018

[104] Kaiyu Y, Fushan L, Jianhua Z, Chandrasekar Perumal V, Tailiang G. All-solution processed semi-transparent perovskite solar cells with silver nanowires electrode. Nanotechnology. 2016;**27**(9):095202

[105] Conings B, Baeten L, De Dobbelaere C, D'Haen J, Manca J, Boyen HG. Perovskite-based hybrid solar cells exceeding 10% efficiency with high reproducibility using a thin film sandwich approach. Advanced Materials. 2014;**26**(13):2041-2046