Upscaling Solution-Processed Perovskite Photovoltaics

Fu Yang,∗ Dongju Jang, Lirong Dong, Shudi Qiu, Andreas Distler, Ning Li, Christoph J. Brabec, and Hans-Joachim Egelhaaf∗

The performance of hybrid organic–inorganic perovskite solar cells has reached a certified efficiency of 25.5% over the past decade, which has attracted significant attention as a promising candidate for photovoltaic (PV) applications. However, the most efficient perovskite solar cells were produced by the technique of spin coating, which is extremely limited in terms of upscaling production for the commercialization of the technology. Furthermore, the efficiencies of large-area perovskite modules are still significantly lower than those of lab size solar cells. Thus, there are still some challenges that need to be overcome to bridge the efficiency gap between small-area perovskite solar cells and large-area perovskite devices. The first challenge lies in preparing high-quality perovskite layers by low-cost and scalable techniques with high reproducibility. Second, selecting and depositing charge extraction layers as well as bottom and top electrodes by scalable and low-cost techniques are essential tasks. In this review, recent progress and challenges of scalable technologies for solution-based coating and printing of perovskite PVs are summarized and analyzed. Based on the analysis, strategies and opportunities are proposed to promote the development of stable and efficient large-area perovskite PV toward commercialization.

1. Introduction

In the past decade, hybrid organic–inorganic perovskite photovoltaics (PVs) have shown a tremendous rise in power conversion efficiency (PCE) from 3.8% to 25.5% (Figure 1a), thus enhancing the opportunities of providing cheap renewable energy supply by PV.[1,2] However, high efficiencies are not sufficient for a PV technology to provide around half of the world’s electricity consumption.[3,4] Two conditions must be met: first, the technology of energy generation needs to be cost-competitive with existing technologies, e.g., fossil fuels or silicon (Si) PV; second, the output of PV manufacturing should be ramped up sustainably.[5]

The price per unit of energy, which is called levelized cost of energy (LCOE) is used to capture cost competitiveness.[6] Several cost model calculations have shown that perovskite LCOE can keep up with silicon and cadmium telluride (CdTe) PV, if the requirements of the magic triangle of PV, i.e., high efficiency, low cost, and long lifetime, are met simultaneously.[6–9] As for lifetime, ≈20 years under operational conditions are typically assumed for LCOE calculations.[10] Although more than 10 000 h of $T_{80}$ lifetime (the time at which efficiency has decayed to 80% of the initial value) have been demonstrated for perovskite solar cells under controlled conditions,[11] the error bar is rather large for this variable, due to the lack of long-term experience with the outdoor operation of perovskite PV modules. On the efficiency side, PCE values of at least 16% should be achieved for large-area modules to reach competitive LCOE values.[6] Concerning material costs, the general message of all relevant cost studies is very clear, albeit the numerical results may vary in detail.[6] Only materials of low to moderate cost are acceptable for perovskite solar modules in order to be cost-competitive to today’s silicon technology (Figure 1c). This applies especially to the hole transport layers (HTLs), thus excluding materials such as 2,2′,7,7′-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9′-spirobifluorene (spiro-OMeTAD), which has been used frequently in efficient lab cells. Even less expensive materials such as poly(3-hexylthiophene-2,5-diyl) (P3HT) add substantially to the bill of materials (BOMs).[12] Furthermore, there is a serious conflict with the other vertices of the magic triangle, especially concerning lifetime requirements: the choice of electrode materials for perovskite devices is strongly reduced, because silver and many other metals are prone to corrosion by iodine,
whereas relatively stable alternatives such as Au are not viable under cost aspects. This leaves mainly carbon-based materials as alternatives. Packaging materials also add substantially to the BOM. Glass packaging increases the BOM by about 2 · 10^2 $ m^2. For flexible packaging, the situation is more serious, as flexible barrier materials which meet the water vapor transmission rate (WVTR) requirements of max. 10^-5 g m^-2 day^-1 for long lived modules will add up to 80 $ m^2.\[4\]

With respect to the second condition, silicon and CdTe PV are unfavorable technologies, because they require too much capital expenditure to increase the output of modules at the rate needed to satisfy the climate goals. While the contribution of the cell to LCOE is low, the system LCOE, module capex and cell capex are relatively high and thus determine the selling price of the silicon modules.\[9\] Perovskite PV has the potential of greatly reducing the capital expenditure for large-scale production by the consequent application of solution processing.\[10\] A model proposed by Bruening et al. reported that reducing capital expenditure by an order of magnitude compared with silicon can achieve a sustainable growth rate of ≈20% annually.\[9\] In addition, the energy payback time of perovskite photovoltaics is much shorter than that of CdTe and Si PVs. To exploit this potential, solution methods which are compatible with high throughput manufacturing are needed. While high throughput production may lower specific manufacturing costs by around one-third, capex per unit can be reduced by up to a factor of ten. However, the production of perovskite solar cells by the most popular technique of spin coating and subsequent thermal annealing is extremely limited in terms of throughput.

To date, the scientific community has been committed to material development to increase PCE and lifetime. However, almost all reported devices are fabricated by methods involving nonscalable steps such as solvent exchange, spin coating, and time and energy consuming annealing processes. While efficiencies exceeding 20% have become state of the art with small area lab cells, substantial PCE losses occur upon transfer to high throughput compatible manufacturing methods, large-area modules, and affordable materials (Figure 1b). Thus, the development of scalable manufacturing techniques is needed for the successful commercialization of perovskite PV. In this review, after an introduction to perovskite film formation as well as of the coating and printing methods available for upscaling, we analyze the current progress in scalable technologies for solution-based preparation of large-area perovskite PVs. Based on our analysis, we will point out the major challenges in closing the efficiency gap between small-area perovskite solar cells and large-area perovskite devices. The first challenge refers to how to prepare high-quality perovskite layers by scalable methods with high reproducibility; the second one consists in selecting and depositing charge extraction/transport layers as well as bottom and top electrodes by cost-effective scalable methods and from inexpensive materials; the third one is about how to optimize the perovskite module design to achieve high photovoltaic performance.

2. Perovskite Nucleation and Crystal Growth

Pinhole-free and homogeneous high-quality perovskite films on large areas are greatly needed for the upscaling of perovskite PVs.\[13\] Therefore, exploring film growth mechanisms and controlling perovskite film formation play an important role to bridge the efficiency gap between small-area perovskite solar cells and large-area perovskite devices. In this section, we will rationalize the importance of solvent evaporation rate for perovskite film formation based on the LaMer concept. The LaMer graph shown in Figure 2a is commonly used to describe the overall nucleation and crystal growth during film formation based on changing concentration.\[14\] When the solvent keeps evaporating, the concentration of the solution will reach a saturated concentration (t), but it cannot produce nuclei because
it must overcome a certain energy barrier. However, when the concentration increases beyond the saturated concentration and reaches the critical concentration ($C_c$) at time ($t_2$), nuclei will be produced and crystals will start growing. As long as the concentration of the solution remains above the critical concentration, the generation of nuclei will continue, along with the growth of existing nuclei to crystals. On one hand, due to the continuous evaporation of the solvent, the concentration of the solution increases continuously and consequently the rate of nuclei generation increases as well. On the other hand, the rates of nuclei generation and crystal growth will be retarded as the materials in the solution are consumed continuously by these processes. Finally, as the concentration of the solution falls back below the critical concentration, the nuclei generation rate will fall to zero at a given time ($t_3$). However, crystals will still grow continuously until the concentration of the solution reaches the saturated concentration ($C_s$). On this background, two cases of drying of the perovskite precursor solution on a substrate can be distinguished. If evaporation of the solvent is slow, the concentration will remain between the critical concentration and the saturated concentration. Consequently, the crystals will keep growing until all solvent is removed while no more nuclei are generated. This will result in the unhindered branch or pin type crystal growth of few nuclei at the substrate surface. This type of crystal growth is not able to cover completely the substrate and will create many defects in the final perovskite film. On the other hand, when the drying of the film is dominated by the fast evaporation of the solvent, the critical concentration is maintained despite the high consumption rate of solute. Therefore, the precursor solution on the substrate will keep creating nuclei until there is no more space on the substrate to accommodate further nuclei, resulting in a uniform dense perovskite layer with small crystal sizes and no defects.[16] Concomitant Ostwald ripening will result in larger average crystal sizes as larger crystals grow at the expense of smaller ones.[16] As a consequence of these considerations, the fast removal of the solvent is a prerequisite for high-quality film formation. While this is relatively easy for small area lab cells, it becomes increasingly difficult for larger areas, even more so as a high level of film homogeneity is required for high efficiency modules.

3. Techniques for Upscaling

Owing to the chemical nature of organometallic halide perovskites, perovskite PV modules can be processed from solution, which is compatible with roll-to-roll (R2R) manufacturing and thus is capable of providing the high throughput required for enabling competitive values of LCOE. At laboratory scale, the most common solution-based process is spin-coating, which has provided the most efficient devices, with a certified PCE of over 25% being the present world record. The main merit of the spin-coating technique is that it can easily deposit high-quality perovskite thin films of well-defined thicknesses and different compositions. However, the thickness and morphology of perovskite films are determined by the continuous centrifugal force arising from spinning, which is difficult to replicate in scalable deposition processes and is thus incompatible with sheet-to-sheet (S2S) and R2R manufacturing. Therefore, alternative techniques that are scalable and can be easily transferred to S2S or R2R manufacturing need to be explored to meet the requirements of commercialization.
As obvious from LCOE considerations, scalable deposition methods need to meet three main requirements: first of all, they need to deliver values of efficiency, which are at least comparable to those achieved by spin coating. Second, they need to maintain a high level of efficiency when going from small lab cells to large-area modules. Last, but not least, they need to be compatible with high throughput production processes, either S2S, or, more preferably, R2R. Therefore, alternative techniques, e.g., doctor-blade coating, slot-die coating, spray coating, and inkjet printing, are more appropriate candidates than spin coating for upsampling perovskite manufacturing (Figure 2b).

Blade coating is the most frequently employed process next to spin coating in lab-scale experiments for fabricating films of well-defined thickness. A wet film of constant thickness, at least for short coating distances, is deposited by spreading ink over the substrate by moving an applicator (the so-called “knife” or “blade”). The thickness of the resulting film is determined by various factors, such as the distance between the blade and the substrate (“slit”), the speed of the applicator, the concentration, surface tension, and viscosity of the solution as well as the substrate properties. With very little waste of ink during the process, efficiencies above 19% at common cell size have been reported.

While the integration of blade coating into R2R equipment is difficult, it can serve as a scale-up analog to another meniscus method, the slot-die coating process, which works similarly to blade coating, except that a slit in the slot die head allows continuous ink supply for continuous film deposition. In contrast to blade coating, the thickness of the film can be precisely defined by adjusting the ink-feeding rate and the speed of the slot die head with respect to the substrate. Galagan and co-workers have demonstrated large-area modules of 12.5 × 13.5 cm² by slot-die coating, showing a PCE over 10% with a power output of 1.7 W.

Screen printing is a common printing method, which could also be investigated for PVs. In screen printing, the ink is applied on the substrate through a screen, which has a specific pattern. At portions of the screen where open portions ink is transferred to the substrate in a desired pattern by squeezing material upon passing an applicator (“squeegee”). This can form a very accurate pattern with resolutions in the 20–100 µm range. The films made through screen printing are mainly of around 1–10 µm thickness, depending on the thickness of the screen, and are commonly applied to form electrodes or mesoscopic scaffolds supporting the active layer.

Screen printing is limited to rather highly viscous ink systems, and is therefore dominantly applied for printing electrodes. In 2017, a 2D/3D (HOOC(CH₂)₄NH₃)₂PbI₄/CH₃NH₃PbI₃ perovskite junction layer was obtained by screen printing for the fabrication of a 10 × 10 cm² perovskite module with a PCE of 11.2% by Graetzel and co-workers.

In contrast to the methods described above, inkjet printing is a noncontact method for manufacturing electronic devices. It uses an array of fine nozzles to deposit small droplets of the precursor solution to form a film with a controlled pattern. Several features, including droplet size and trajectory as well as printing speed, can influence the final films. The limited printing speed can be compensated by parallelization of print heads, as in other inkjet applications. Recently, Abzieher et al. inkjet printed a mixed cations cesium (Cs), formamidinium (FA), and methylammonium (MA) Csₓ(FAXMA₀.8₇Pb(Br₀.₅I₀.₉₅)₃ perovskite layer on top of an undoped electron-beam-evaporated nickel oxide (NiOₓ) hole transport layer, showing a PCE of 20.7%, thus proving that inkjet printing perovskite layers is competitive with spin-coating (Figure 3), which in this experiment yielded devices with an efficiency of 17.7%. However, there is still a lack of research on suitable perovskite coating conditions or ink compositions. In any printed PV device, the maximum achievable efficiency is highly dependent on the active layer quality. One of the biggest challenges in inkjet printing of perovskite solar cells (PSCs) is the rate of solvent evaporation and perovskite crystallization. Inkjet inks are usually slowly drying to achieve good process stability and sufficient nozzle open times. However, using such slowly drying solvents may counteract the development of optimized active layer microstructures. Most reports on inkjet-printed PSCs focus on MAPbI₃, because it is the best investigated material in the field and offers various ways to influence the morphology of the deposited films. In 2014, Yang and co-workers printed MAPbI₃ perovskite layers in a two-step process, showing a PCE of 11.6%. In the same year, the first one-step process was introduced by Song and co-workers, who printed precursors prepared with γ-butyrolactone (GBL) as solvent onto mesoscopic TiO₂. They showed a PCE of 12.3%. Later, Mathies et al. published cells with a PCE of 11.3%, showing improved open-circuit voltage (V_oc) through applying a vacuum in the annealing process to improve crystallization of the perovskite. In 2020, Paetzold and co-workers inkjet-printed triple-cation Cs₀.₃₀FA₀.₇₅MA₀.₁₅Pb(Br₀.₁₅I₀.₈₅)₃ perovskite layers with exceptional thicknesses of 1.5 µm by solvent engineering and using a vacuum to increase the evaporation rate of the solvents, thus enabling unprecedented PCEs of 21.6% of inkjet-printed devices, which are comparable to those of spin-coated devices.

Spray coating also uses a fine nozzle to spread small ink droplets over a large area. The methods of forming fine sols can be classified into several categories: pneumatic spray (through fast gas flow), ultrasonic spray (through ultrasonic vibration), or electrospray (through electrical repulsion). Pneumatic spray and ultrasonic spray methods have already been used to deposit inorganic oxide layers for supporting the perovskite active layer. In the case of perovskite layers, ultrasonic spray has been employed. For spray coating, the biggest advantage is that it can coat quickly over a very large area. However, the sizes of the ink droplets ejected from the nozzle are very diverse and the ink droplets can be easily overlapped on the substrate, affecting the final film thickness. In addition, the thickness of the ink droplets deposited on the already formed perovskite will destroy the existing layer, thereby affecting the crystal quality. Efforts to reduce those effects have also been done mainly by keeping the temperature of the substrate very high to evaporate rapidly the solvent, thus avoiding the damage of the underneath layer.

4. State of the Art of Large-Area High-Quality Perovskite Devices

As has been shown in Figure 1b, the PCEs of perovskite modules are still significantly lower than those of small area lab
cells. However, high film uniformity of the perovskite layer over large areas is one of the main requirements the scale-up technology. Thus, measuring the performance of larger PSCs (over 1 cm²) is mandatory for judging the potential of coating, quenching, and post-treatment methods for upscaling. In the following, we will therefore give a brief overview of the efficiency development of devices with an area over 1 cm². Table 1 summarizes the performances of large-area perovskite solar cells and solar modules based on different coating techniques. In 2014, the Di Carlo group fabricated a mesoporous structure MAPbI₃₋ₓClₓ perovskite solar module, which showed a PCE of 5.1% on an active area of 16.8 cm² (if not mentioned otherwise, all efficiency values in this section refer to the active area), using both P3HT and spiro-OMeTAD as HTL.[33] Later, the Seok group first reported the fabrication of a planar 10 × 10 cm² MAPbI₃ solar module (60 cm²), showing 8.7% PCE by using [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM)/lithium fluoride (LiF) as the electron transport layer (ETL).[34] In September of 2014, the Di Carlo group developed innovative and scalable patterning procedures to minimize the series resistance of the interconnections of a MAPbI₃₋ₓClₓ perovskite solar module prepared by two-step deposition to increase its PCE to 13% (10.08 cm²).[35] In 2015, PSC modules were fabricated through blade-coating with a PCE of 10.4% (10.1 cm²) and 4.3% (100 cm²) by Di Carlo and co-workers.[36] Through adopting poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS) and PC₆₁BM as HTL and ETL in the p–i–n structure for better charge injection/separation, the Im group prepared a 100 cm² MAPbI₃ solar module (40 cm²), which exhibited a PCE of 12.9%.[37] Later, the Han group developed a MAPbI₃ perovskite solar cell with a doped inorganic charge extraction layer (LiMgNiO) for rapid carrier extraction, which could achieve a PCE of over 15% with an aperture area of 1.02 cm².[38] In 2016, through the addition of chloride to improve the morphology of the film by reducing the crystallization rate of the perovskite and of bromide to increase V_OC, Wu and co-workers fabricated a MAPbI₃₋ₓBrₓClₓ perovskite solar module by one-step hot solution spin-coating, showing a PCE of up to 14.3% with an active area of 25.2 cm².[39] In September of 2016, the Han group fabricated FA₀.₈₅MA₀.₁₅Pb(I₀.₈₅Br₀.₁₅)₃ perovskite solar cells with a certified PCE of 18.21% (1.022 cm²) by engineering the perovskite–fullerene heterojunction structure to improve photoelectron collection and reduce recombination losses.[40] In 2017, as described in Figure 4, through combining...
Table 1. Representative reports of large-area PSCs (≥1 cm²) or PSMs by different coating methods sorted by year. Note: c-TiO: compact TiO₂; m-TiO₂: mesoporous TiO₂.

| Device category | Device architecture | Perovskite fabrication method | Strategy to control perovskite film quality | Area [cm²] (module/active area) | V_{OC} [V] | J_{SC} [mA cm⁻²] | I_{SC} [mA cm⁻²] | FF [%] | PCE [%] | Refs. |
|-----------------|---------------------|-------------------------------|--------------------------------------------|--------------------------------|------------|-------------------|-------------------|-------|--------|-------|
| Cell            | FTO/NiMgLiO/MAPbI₃/PC₆₁BM/Ti(Nb)Oₓ/Ag | Spin-coating (one-step) | Antisolvent | −/1.02 | 1.09 | 17.35 | 66.8 | 15 | [38] |
| Cell            | FTO/SnO₂/(MAPbBr₃)₀.₁₅(FAPbI₃)₀.₈₅/spiro-OMeTAD/Au | Blade-coating (one-step) | Gas quenching | −/1.0 | 1.15 | 22.65 | 69.47 | 18.02 | [150] |
| Cell            | ITO/NiOₓ/MAPbI₃/PC₆₁BM-PND(20D)T₂/Ag | Spray-coating | | −/1.0 | 0.93 | 19.3 | 56.80 | 10.09 | [151] |
| Cell            | ITO/c-TiO₂/PMMA/PC₆₁BM/Cs₉₀.₁₉FA₈₄.₉₁PbI₂₂₃.₆₁/P3HT:CuPc/Au | Spin-coating (one-step) | Vacuum | −/1.0 | 1.232 | 21.835 | 83.6 | 22.489 | [152] |
| Cell            | FTO/c-TiO₂/MAPbI₃/spiro-OMeTAD/Au | Spin-coating (one-step) | Antisolvent | −/1 | 1.12 | 20.5 | 68.0 | 14.6 | [153] |
| Cell            | FTO/c-TiO₂/FAPbI₃/spiro-OMeTAD/Au | Chemical vapor deposition | | −/2 | 1.02 | 19.5 | 53 | 10.4 | [153] |
| Cell            | FTO/NiOₓ/FA₈₂₅MA₀.₈₅PbI₃.₅₁/PC₆₁BM/Ag | Spin-coating (one-step) | Additive | −/1.022 | 1.08 | 21.95 | 78.4 | 18.21 | [40] |
| Cell            | ITO/PEDOT:PSS/MAPbI₃/PC₆₁BM/C₆₀/BCP/Au | Spin-coating (two-step) | Additive + vapor anneal | −/1.3 | 0.99 | 22.51 | 75.0 | 16.7 | [154] |
| Cell            | FTO/c-TiO₂/MAPbI₃/spiro-OMeTAD/Au | Spin-coating (one-step) | Antisolvent | −/1.08 | 1.17 | 21.28 | 75.7 | 19.5 | [42] |
| Cell            | Cell FTO/c-TiO₂/MAPbI₃/spiro-OMeTAD/Au | Spin-coating (one-step) | Additive | −/1.025 | 1.12 | 23.17 | 75.7 | 19.19 | [43] |
| Cell            | FTO/c-TiO₂/FAPbI₃/spiro-OMeTAD/Au | Spin-coating (two-step) | Additive | −/1 | 1 | 24.7 | 72.3 | 19.7 | [44] |
| Cell            | ITO/SnO₂/(FAPbI₃)₀.₁₅(MAPbBr₃)₀.₈₅/spiro-OMeTAD/Au | Spin-coating (two-step) | | −/1 | 1.12 | 23.45 | 76.85 | 20.12 | [45] |
| Cell            | ITO/PEDOT:PSS/FAPbI₃/PC₆₁BM/Ag | Spin-coating (two-step) | – | 1.2 | 1.05 | 22.35 | – | 64.9 | 15.23 | [156] |
| Cell            | Cell FTO/NiOₓ/FA₈₂₅MA₀.₈₅PbI₃.₅₁/PC₆₁BM/Ag | Spin-coating (one-step) | Additive | −/1 | 1.01 | 21.7 | 67.15 | 14.72 | [157] |
| Cell            | FTO/c-TiO₂/MAPbI₃/spiro-OMeTAD/Au | Blade-coating (one-step) | Gas quenching | −/1 | 1.09 | 21.3 | 66.1 | 15.3 | [79] |
| Cell            | FTO/c-TiO₂/FAPbI₃/spiro-OMeTAD/Au | Blade-coating (one-step) | High temperature (150 °C) | 1.0 | 1.08 | 23.17 | 68.49 | 17.06 | [163] |
| Cell            | FTO/c-TiO₂/FA₈₂₅MA₀.₈₅PbI₃.₅₁/C₆₀/BCP/Au | Blade-coating (one-step) | High temperature (145 °C) | 1.0 | 1.15 | 22.3 | 71.3 | 18.3 | [158] |
| Cell            | FTO/NiOₓ/MAPbI₃/PC₆₁BM/BCP/Ag | Soft-cover deposition (one-step) | – | 2 | 1.62 | 21.8 | 87.8 | 17.6 | [160] |
| Cell            | FTO/c-TiO₂/m-TiO₂/MAPbI₃/spiro-OMeTAD/Au | Soft-cover deposition (one-step) | – | 50 | 1.12 | 22.6 | 76.2 | 19.3 | [161] |
| Cell            | FTO/NiOₓ/MAPbI₃/PC₆₁BM/BCP/Ag | Soft-cover deposition (one-step) | – | 80 | 1.03 | 21.5 | 70.1 | 15.5 | [62] |
| Cell            | FTO/c-TiO₂/MAPbI₃/spiro-OMeTAD/Au | Spin-coating (one-step) | Antisolvent | −/1.2 | 1.09 | 21.3 | – | 66.1 | 15.3 | [79] |
| Cell            | FTO/c-TiO₂/MAPbI₃/spiro-OMeTAD/Au | Spin-coating (two-step) | Spray coating (60 °C) | −/1.0 | 1.032 | 18.9 | 68.0 | 13.09 | [161] |
| Cell            | ITO/PDDOT:PSS/FAPbI₃/CTAB-doped PC₆₁BM/Au | Spin-coating (two-step) | – | 1.03 | 20.70 | – | 72.34 | 15.42 | [162] |
| Cell            | FTO/c-TiO₂/m-TiO₂/MAPbI₃/spiro-OMeTAD/Au | Spin-coating (one-step) | Vacuum | −/1 | 1.143 | 22.06 | – | 67.0 | 19.6 | [61] |
| Cell            | FTO/c-TiO₂/MAPbI₃/spiro-OMeTAD/Au | Blade coating (one-step) | Gas quenching | −/1 | 1.09 | 17.62 | 61.2 | 11.7 | [163] |
| Cell            | ITO/SnO₂/MAPbI₃/spiro-OMeTAD/Au | Blade coating (one-step) | Gas quenching | −/1 | 1.08 | 23.32 | 75.92 | 19.12 | [164] |
| Module          | FTO/c-TiO₂/m-TiO₂/MAPbI₃/C₆₀/spiro-OMeTAD/Au | Spin-coating (one-step) | – | −/16.8 | 4.31 | 32.9 | 60.3 | 5.1 | [33] |
| Device category | Device architecture | Perovskite fabrication method | Strategy to control perovskite film deposition | Area [cm²] (module/active area) | Voc [V] | Jsc [mA cm⁻²] | PCE [%] | FF [%] | Refs. |
|-----------------|---------------------|-------------------------------|----------------------------------------------|-------------------------------|---------|--------------|--------|-------|-------|
| Module          | ITO/PEDOT:PSS/MAPbI₃/PC₆1BM/LiF/Al | Spin-coating (one-step) | Antisolvent | 100/60 | 0.87 | 20.7 | 78.3 | 8.7 | [34] |
| Module          | FTO/c-TiO₂/MAPbI₃,Cl₃/P3HT/Au | Spin-coating (two-step) | Gas quenching | –/10.08 | 3.36 | 13.4 | 77.8 | 13.0 | [35] |
| Module          | ITO/c-TiO₂/m-TiO₂/MAPbI₃,Cl₃ /spiro-OMeTAD/Au | Spin-coating (one-step) | – | –/0.92 Flexible | 3.39 | 5.2 | 71 | 3.1 | [97] |
| Module          | ITO/PEDOT:PSS/MAPbI₃/PC₆1BM/Au | Spin-coating (one-step) | – | 100/40 | 10.1 | 80.1 | 63.7 | 12.9 | [37] |
| Module          | FTO/c-TiO₂/m-TiO₂, nanorods/MAPbI₃,Cl₃/spiro-OMeTAD/Au | Spin-coating (one-step) | – | –/10.8 | 3.37 | 22.2 | 57.1 | 10.5 | [165] |
| Module          | ITO/PEDOT:PSS/CH₃NH₃PbI₃₂.7Br₀.₃/PC₆1BM/Ti/PD/Al | Spin-coating (one-step) | – | 25/12 | 2.71 | 6.48 | 63.8 | 11.2 | [166] |
| Module          | FTO/c-TiO₂/MAPbI₃/spiro-OMeTAD/Au | Spin-coating (one-step) | Antisolvent | 25/15.4 | 0.98 | 19 | 46 | 8.5 | [153] |
| Module          | FTO/c-TiO₂/FAPbI₃/spiro-OMeTAD/Au | Chemical vapor deposition | – | 25/15.4 | 0.77 | 15.2 | 49 | 5.8 | [153] |
| Module          | ITO/PEDOT:PSS/MAPbI₃₋ₓBrₓClₓ(PC₆1BM/Ca)₂/Au | Spin-coating (one-step) | Hot solution (60 °C) | –/25.2 | 9.05 | 74.4 | 14.3 | [39] |
| Module          | FTO/c-TiO₂/m-TiO₂/(FAPbI₃)₀.₉₅(MAPbI₃)₀.₀₅/PC₆1BM/P3HT/Au | Spin-coating (one-step) | Antisolvent | 25/24.97 | 8.78 | 2.72 | 71.7 | 17.1 | [47] |
| Module          | FTO/c-TiO₂/m-TiO₂/(CsPbI₃)₀.₉₅(FAPbI₃)₀.₀₅(MAPbI₃)₀.₁₅/P3HT/Au | Spin-coating (one-step) | Antisolvent | 156.25/108 | 10.46 | 173.78 | 65.08 | 13.56 | [167] |
| Module          | FTO/c-TiO₂/MAPbI₃/spiro-OMeTAD/Au | Doctor-blading (one-step) | Additive + antisolvent | 12.6/11.09 | 6.64 | 11.5 | 14.06 | [135] |
| Module          | FTO/c-TiO₂/m-TiO₂/MAPbI₃/spiro-OMeTAD/Au | Blade coating (two-step) | Gas quenching | –/10.08 | 4.11 | 17.1 | 43.27 | 58.14 | 10.26 | [168] |
| Module          | FTO/SnO₂₉₁₀Cs₂₁₀(FAPbI₃)₀.₈₅(MAPbI₃)₀.₁₅/Pb₁₀₁₅₈₅/C₆₁BM/spiro-OMeTAD/Au | Spin coating (one-step) | Antisolvent | 25/10 | 6.496 | 3.07 | 62 | 12.40 | [169] |
| Module          | ITO/PTAA/MAPbI₃/Cao/BCP/Au | Doctor-blading (one-step) | High temperature (145 °C) + additive | 110.5/57.8 | 17.24 | – | 72.5 | –68.9 | 14.9 | [170] |
| Module          | ITO/PTAA/MAPbI₃/Cao/BCP/Au | Doctor-blading (one-step) | Additive + vacuum | 16/10.08 | 3.87 | 4.93 | 59 | 11.25 | [179] |
| Module          | FTO/SnO₂₉₁₀Cs₂₁₀(MAPbI₃)₀.₅₅/Mb₁₀₁₅₈₅/spiro-OMeTAD/Au | Doctor-blading (one-step) | Gas quenching | 25/16 | ≈8.8 | ≈2.2 | ≈71.5 | 13.85 | [177] |
| Module          | ITO/PTAA/MAPbI₃/Cao/BCP/Cu | Doctor-blading (one-step) | Gas quenching + additive | /42.9 | 13.14 | 19.71 | 73.5 | 15.86 | [172] |
| Module          | ITO/ZnO/MAPbI₃/P3HT/Au | Slot-die coating (two-step) | Gas quenching | /47.3 | 4.35 | 10.2 | 51.1 | 4.56 | [173] |
| Module          | ITO/C₆₁TMAC₃N₃PC₆₁BM/BCP/Au | Slot-die coating (one-step) | – | 149.5/142 | 21.2 | 17.3 | 116 | 67.9 | 11.8 | [20] |
| Module          | ITO/C₆₁TMAC₃N₃PC₆₁BM/BCP/Au | Doctor-blading (one-step) | Gas quenching | /168.75/151.9 | 20.8 | 19 | 114 | 70.6 | 11.1 | [20] |
| Module          | ITO/PTAA/MAPbI₃/Cao/BCP/Au | Doctor-blading (one-step) | Gas quenching | /63.7 | 18.9 | 74.5 | 76.2 | 16.9 | [37] |
| Module          | ITO/PTAA/MAPbI₃/Cao/BCP/Au | Doctor-blading (one-step) | Gas quenching | /703 | 14.36 | 15.83 | 75.8 | 11.7 | [174] |
| Module          | ITO/PTAA/MAPbI₃/Cao/BCP/Au | Doctor-blading (one-step) | Gas quenching | /802 | 15.83 | – | 68.0 | 11.6 | [174] |
| Module          | ITO/NiO₂₁₇/CH₃NH₃PbI₃₋ₓBrₓ/C₆₁BM/BCP/A | Meniscus coating (one-step) | Gas quenching | 26.7/25 | 4.5 | 4.4 | – | 75 | 15 | [175] |
| Module          | FTO/c-TiO₂/m-TiO₂/m-ZrO₂/Carbon/ (HOOC(CH₂)₃NH₃)₂(PbI₃)₂ | Screen printing (one-step) | – | 50/31 | 3.72 | 19.6 | – | 57.5 | 10.46 | [176] |
| Module          | FTO/c-TiO₂/m-TiO₂/m-ZrO₂/Carbon/ (HOOC(CH₂)₃NH₃)₂(PbI₃)₂ | Screen printing (one-step) | – | 100/70 | 9.63 | 17.72 | 62.9 | 10.74 | [176] |
| Module          | FTO/c-TiO₂/m-TiO₂/m-ZrO₂/Carbon/ (HOOC(CH₂)₃NH₃)₂(PbI₃)₂ | Screen printing (one-step) | – | 100/49 | 9.3 | 23.0 | 53 | 10.4 | [177] |
| Module          | FTO/c-TiO₂/m-TiO₂/m-ZrO₂/Carbon/ (HOOC(CH₂)₃NH₃)₂(PbI₃)₂ | Screen printing (one-step) | – | /198 | 18.2 | 0.5 | 38.9 | 3.2 | [178] |
Table 1. Continued.

| Device category | Device architecture | Perovskite fabrication method | Strategy to control perovskite film quality | Area [cm$^2$] | $V_{OC}$ [V] | $J_{SC}$ [mA cm$^{-2}$] | $FF$ [%] | PCE [%] | Refs. |
|-----------------|---------------------|-----------------------------|-----------------------------------------------|-------------|-------------|----------------------|--------|--------|-------|
| Module          | FTO/c-TiO$_2$/m-TiO$_2$/MAPbI$_3$/spiro-OMeTAD/Au | Soft-cover deposition (one-step) | 50 °C | 36.13 | 8.36 | 73 | 71.5 | 12.1 | [161] |
| Module          | ITO/TiO$_2$/MAPbI$_3$/GO-Li/MAPbI$_3$/spiro-OMeTAD/Au | Spray coating (one-step) | 50 °C | 3.8 | 3.31 | – | 19.4 | 70.0 | 11.7 | [163] |
| Module          | FTO/c-TiO$_2$/m-TiO$_2$/GO-Li/MAPbI$_3$/spiro-OMeTAD/Au | Spin-coating (two-step) | 100/50.6 | 8.57 | – | 114.8 | 64.6 | 12.6 | [179] |
| Module          | FTO/SnO$_2$/K$_{x}$Cs$_{y}$FA$_{1-x}$Br$_{y}$/spiro-OMeTAD/Au | Spin-coating (one-step) | Antisolvent | 36/20 | 6.804 | 3.52 | 65 | 15.58 | [180] |
| Module          | FTO/c-TiO$_2$/FA$_{1-x}$Pb$_x$I$_3$/spiro-OMeTAD/Au | Spin-coating (one-step) | Antisolvent | –/16 | 1.13 | 17.3 | – | 61.9 | 12.1 | [181] |
| Module          | FITO/ZnO/MAPbI$_3$/carbon | Slot-die coating (one-step) | Vacuum | 25/17.6 | 6.14 | 3.25 | – | 53 | 10.6 | [182] |
| Module          | FTO/SnO$_2$/C$_{60}$/ZnO$_2$/FA$_{1-x}$Pb$_x$I$_3$/spiro-OMeTAD/Au | Chemical vapor deposition | 100/91.8 | 13.55 | 1.42 | | 59.6 | 10.37 | [183] |
| Module          | FTO/SnO$_2$/C$_{60}$/ZnO$_2$/FA$_{1-x}$Pb$_x$I$_3$/spiro-OMeTAD/Au | Chemical vapor deposition | 64/41.25 | 9.18 | 2.25 | | 52.8 | 12.24 | [184] |
| Module          | ITO/TiO$_2$/Cs$_{60}$/FA$_{1-x}$Pb$_x$I$_3$/spiro-OMeTAD/Au | Chemical vapor deposition | 25/12 | 5.84 | 3.67 | | 68.1 | 14.6 | [180] |
| Module          | FTO/TiO$_2$/FA$_{1-x}$Pb$_x$I$_3$/spiro-OMeTAD/Au | Chemical vapor deposition | 25/12 | 6.29 | 3.55 | | 66 | 14.7 | [185] |
| Module          | PEN/ITO/SnO$_2$/ZnO/SnO$_2$/FA$_{1-x}$Pb$_x$I$_3$/spiro-OMeTAD/Au | Spin-coating (one-step) | Antisolvent | 100/90/202.5 | 16.6 | 1.44 | | 74.83 | 17.9 | [186] |
| Module          | FTO/TiO$_2$/FA$_{1-x}$Pb$_x$I$_3$/spiro-OMeTAD/Au | Slot-die coating (one-step) | Gas quenching | 16/10.2 | 5.44 | – | 45.6 | 76.4 | 18.6 | [187] |
| Module          | ITO/SnO$_2$/C$_{60}$/MAPbI$_3$/PC$_{61}$BM/TBAOH/Ag | Slot-die coating (one-step) | Near-infrared irradiation heating | 16/7.92 | 4.55 | – | 44.8 | 76.2 | 19.6 | [188] |
| Module          | ITO/2T-NATA/MAPbI$_3$/C$_{60}$/BCP/Ag | Flash-evaporation (two-step) | 31.2/16.0 | 7.95 | 2.58 | | 64.1 | 13.15 | [189] |
| Module          | FTO/SnO$_2$/FA$_{1-x}$Pb$_x$I$_3$/spiro-OMeTAD/Au | D-bar coating (one-step) | Gas quenching | 25/19.69 | 10.816 | 2.15 | | 77.2 | 17.94 | [190] |
| Module          | ITO/PTAA/MAPbI$_3$/C$_{60}$/BCP/Ag | Spin-coating | Antisolvent | –/6.8 | 4.45 | 6.11 | | 72.7 | 19.78 | [191] |
| Module          | ITO/SnO$_2$/C$_{60}$/FA$_{1-x}$Pb$_x$I$_3$/spiro-OMeTAD/Au | Spin-coating, vapor deposition | 25/22.4 | 7.31 | 2.96 | | 67.23 | 14.55 | [192] |
| Module          | ITO/PTAA/PFN-Br/MAPbI$_3$/PC$_{61}$BM/BCP/Cu | Spin-coating | Antisolvent | –/9.06 | 3.38 | 6.64 | | 60.19 | 69 | 15.52 | [193] |
| Module          | ITO/TiO$_2$/Cs$_{60}$/FA$_{1-x}$Pb$_x$I$_3$/spiro-OMeTAD/Au | Spin-coating | Vacuum | 36/21.06 | 2.163 | – | 250.60 | 73.11 | 18.82 | [194] |
| Module          | ITO/PTAA/FAPb$_{1-x}$Pb$_x$I$_3$/C$_{60}$/BCP/Cu | Blade-coating | Gas quenching | 30/27.6 | 8.715 | 3.076 | | 83.59 | 75.41 | 20.2 | [51] |
| Module          | ITO/SnO$_2$/C$_{60}$/MAPbI$_3$/P3HT/carbon | Blade-coating | Gas quenching | 25/4.0 | 4.20 | 5.28 | | 69.0 | 15.3 | [177] |

the polyelectrolyte polyethyleneimine (PEI) with PC$_{61}$BM for a stable and printable ETL with enhanced charge extraction, the Lee group prepared a planar MAPbI$_3$ perovskite solar cell with a PCE of up to 18.1% (active area, 1 cm$^2$). At the same time, the Sargent group reported a certified PCE of 19.5% for planar Cs$_{60}$/FA$_{1-x}$MA$_{x}$/Pb$_{1-x}$Br$_x$/Cs$_{60}$ perovskite cells with active areas of 1 cm$^2$ by using chlorin-capped titanium dioxide (TiO$_2$) colloidal nanocrystal films as an electron selective layer to mitigate interfacial recombination and improve interface binding. Later, by introducing methylvanadum acetate and thioselenium-carbazone additive into perovskite precursor solution to grow a uniform and large crystal perovskite layer, the Han group achieved a certified PCE of 19.19% for MAPbI$_3$ perovskite solar cells (active area of 1.025 cm$^2$) (Figure 5). In 2017, by adding iodide ions into formamidinium iodide (FAI) and methylammonium bromide (MABr) isopropanol (IPA) solution to modify the two-step spin-coating method through an intramolecular exchange process and decrease the concentration of deep-level defects, the Seok group fabricated Pb$_{1-x}$/PbBr$_x$/FAI/MABr-based perovskite solar cells with an active area of 1 cm$^2$, showing a certified PCE up to 19.7%.

© 2021 The Authors. Advanced Energy Materials published by Wiley-VCH GmbH
a PCE of up to 20.1%. A 2D/3D (HOOC(CH₂)₄NH₃)₂PbI₄/CH₃NH₃PbI₃ perovskite junction layer was obtained by screen printing for the 100 cm² perovskite module with PCE of 11.2% by Graetzel and co-workers. In 2018, a large module with an aperture area of 168.75 cm² (PCE of 11.1%) has been reported by Galagan and co-workers, prepared by the slot-die coating method. Through inkjet-printing PbI₂ layers on mesoporous TiO₂ and converting them with MAI powder into the MAPbI₃ perovskite, a PSC with an efficiency of 17.72% on 2.02 cm² active area was achieved by Li et al. The Jung group fabricated a large-area high-quality [CsPbI₃]₀.₀₅[(FAPbI₃)₀.₈₅(MAPbBr₃)₀.₁₅]₀.₉₅ perovskite film (14 × 14 cm²) via a spin-coating method using anisole as antisolvent, with a PCE of 17.37% for 1.08 cm² active layer. Compared to other antisolvents (e.g., chlorobenzene), anisole provides an ultrawide process window to fabricate the perovskite thin films. In 2019, through in situ reaction of n-hexyl trimethyl ammonium bromide on the perovskite surface to insert a wide-bandgap halide between (FAPbI₃)₀.₉₅(MAPbBr₃)₀.₀₅ perovskite layer and the P3HT HTL layer for a higher flat-band potential, the Seo group fabricated 5 × 5 cm² modules with PCEs of up to 17.1% (active area, 24.97 cm²). Later, through optimizing the uniform and pinhole-free SnO₂ film by an electrostatic self-assembly method, Lu et al. fabricated 100 cm² [CsPbI₃]₀.₀₅[(FAPbI₃)₀.₈₅(MAPbBr₃)₀.₁₅]₀.₉₅ perovskite modules showing PCEs of 15.3% and 14.03% for the active area of 25 and 100 cm², respectively. Recently, as illustrated in Figure 6, the Di Carlo group fabricated 12.5 × 12.5 cm² perovskite modules by interface engineering mesoporous perovskite solar modules with 2D materials (graphene and functionalized molybdenum(IV)sulfide, MoS₂), showing PCEs of 15.27% (active area 82 cm²) and 13.56% (active area 108 cm²). The function of the 2D materials is to accelerate the electron and hole extraction, thus improving both the stability and the overall power conversion efficiency of the PSCs compared to standard devices. Through tailoring solvent coordination in the doctor-blade coating method, a large module with an aperture area of 63.7 cm² (PCE of 16.4%) has been reported by Deng et al. Recently, through defect compensation with excessive AX (where A is either formamidinium or cesium, and X is iodine), Deng et al. obtained a certified PCE of 20.2% with an active area of 276 cm², along with enhanced stability under light soaking.

From early 2018 to middle 2019, Toshiba Corporation held the world record for the largest MAPbI₃ perovskite film-based submodule with 24.15 × 29.10 cm² (703 cm² designated illumination area; definitions of the measurement areas can be found in refs. [8#8] and [52]) with a certified PCE of 11.7%, an V Oc of 1.073 V, a short-circuit current density (J SC) of 14.36 mA cm⁻², and fill factor (FF) of 75.8% (all the V Oc and J SC values are given per cell in the module). To further enlarge the area from 703 to 802 cm², a perovskite solar module with a certified PCE of 11.6% has been achieved. This large-area submodule and module were fabricated by a two-step process employing meniscus printing technology with PbI₂ and MAI as precursor solutions applied sequentially. It has been mentioned that the goal of the company is to fabricate PV modules with sizes of 900 cm² with which it would be possible to achieve an LCOE of ~0.06 USD kWh⁻¹ by 2030. In 2020, Panasonic Corp. reported a certified efficiency of 16.1% for a module of 802 cm² in size through the inkjet printing method, and later
the efficiency has been increased to 17.9%, which is the current world record certified efficiency for a module with an active area of 802 cm².

Figure 7 gives an overview of activities related to upscaling perovskite PV in terms of materials, architectures and processes, for the periods up to and later than 2018. The trend toward the commercialization of perovskite research is obvious. While there were hardly any reports on devices with more than 200 cm² active area before 2019, 14% of all papers published on devices with 1 cm² active area or more since then cover devices with this area. At the same time, the fraction of publications on perovskite modules has increased from 56%...
to 79%. Accordingly, spin coating, which had been the dominant deposition method before 2019, has been replaced by R2R compatible coating and printing methods. Other obvious trends are observed for quenching methods and perovskite composition. Solvent quenching has lost its status of the most popular quenching method to gas quenching, with vacuum quenching showing up as a promising alternative. The latter two methods have proven to provide reliable high efficiencies if performed correctly, and allow for much more convenient handling, especially in R2R production processes. Mixed-cation perovskite systems have become much more popular, due to their superior stability over that of MAPbI₃. Less obvious trends are observed with respect to the architecture (n–i–p vs p–i–n), the HTL, and the materials for the top electrode. As for the popularity of stack directions, p–i–n has almost caught up to n–i–p, as more and more n-type materials are being developed for deposition on top of the perovskite layer. Despite its high cost and low stability, spiro-OMeTAD (doped with 4-tert-butylpyridine (tBP) and Li salt) is still by far the most popular material for the HTL. For top electrodes, the most preferred material is vapor-deposited metal. Carbon electrodes are still the exception, rather than the rule. This is owed to the many disadvantages carbon electrodes have, despite their outstanding inertness, which are, e.g., their low reflectivity, possible contact resistance to the charge extraction layer, the interaction of the solvent with the layers underneath during deposition, and their porosity, which allows for diffusion of oxygen and water.

5. Strategies of Upscaling of Perovskite Devices

5.1. Strategies for Upscaling Perovskite Layers

The reasons for the significant efficiency gap between small area cells and large-area modules will be explained as follows:[34] 1) The coverage, uniformity, and flatness of the films in the perovskite devices are not perfect due to the solution processing method. Even the perovskite solar cells show efficient performance in a small area, their PCEs still show a wide range of distribution. 2) When the device's size is enlarged, the defects of the perovskite layers are also increased. This will have a greater impact on the extraction and transport of photoinduced carriers, leading to a significant decrease in device performance. 3) The series resistance ($R_s$) of the device increased caused by the sheet resistance of transparent electrode increases approximately linearly as the area increases, leading to a decreased performance. To alleviate this problem, cells have to be separated into modules. While the modules will result in interconnects introducing additional losses of the performance. 4) Until now, most of the efficient perovskite solar cells are fabricated by the spin-coating method, which is limited to the device area due to the inhomogeneous film thickness and morphology. And, transforming the high efficiency perovskite solar cells from conventional spin-coated devices to devices by scalable printing methods is not that straightforward due to the different process and
Antisolvent-based methods have been most commonly used to obtain uniform and homogeneous perovskite films. The antisolvent absorbs the solvent contained in the precursor, whereas the perovskite constituents are insoluble in the antisolvent. Typically, dimethylformamide (DMF), dimethylsulfoxide (DMSO), N-methylpyrrolidone (NMP), GBL, and 2-methoxyethanol (2-ME) are used as solvents of perovskite precursor, while toluene, chlorobenzene, diethyl ether, ethyl acetate, hexane, and anisole are used as antisolvents. Jeon et al. applied toluene as an antisolvent by dripping it onto the wet precursor layer during the spin coating process. However, the antisolvent applied by dripping during spin coating caused complicated physical effects with the wet precursor film throughout the process, resulting in low reproducibility with inhomogeneous surface and pinholes. Ye et al. have developed the conventional method of spraying an antisolvent to produce uniform layers without the physical problems arising from solvent dripping.

In particular, Kim et al. achieved a PCE of 12.1% by spraying antisolvent on 16 cm² large perovskite precursor wet films. However, this method has been tested only for spin coating so far and has turned out to be difficult for upscaling due to inhomogeneous spreading on the substrate, which has negative effects on crystallization. To overcome this problem, a method of dipping a substrate covered by a wet precursor film into a container filled with antisolvent has been developed. Taking the necessary provisions on the equipment side, the dipping process does not have any process limitation with the continuous methods used in R2R manufacturing.

Applying strong gas flow or vacuum has also been used to remove the solvent rapidly. Huang et al. induced rapid crystallization by injecting a strong gas flow onto the substrate with a wet precursor film applied by spin coating. Cotella et al. applied a strong gas flow by an air knife attached to a slot-die coater to fabricate perovskite layers. Li et al. suggested the application of vacuum to accelerate solvent evaporation. With this method, they achieved perovskite layers of around 1 cm², keeping the efficiency at around 20%. By combining both methods, strong vacuum and strong gas flow, Ding et al. developed the process having both advantages. From this method, homogeneous perovskite layers of 1 cm² were generated, the champion large-area PSCs achieving a $J_{SC}$ of 22.56 mA cm⁻², a $V_{OC}$ of 1115 mV, an FF of 67.80%, and a PCE of 17.05%.

Most recently, a method using the formation of a complex between methylamine gas and the MAI and PbI₂ powders can be diluted in a solvent to adjust the viscosity to the appropriate range for the specific coating device. The adducts of the precursors with methylamine are soluble in the low boiling point solvent acetonitrile (ACN), in which perovskites and their precursors are insoluble otherwise. Noel et al. synthesized perovskite precursor solutions having fast evaporation rates by the process described above and achieved 18% efficiency without additional processes such as vacuum or gas quenching. The methylamine process introduced here has been applied to spin coating and doctor-blading. It seems plausible that it can also be applied to other solution coating processes used for upscaling, such as slot-die coating. Especially, it has been reported that exposure of low-quality perovskite crystals...
to methylamine gas results in substantial enhancement of crystallinity.[71]

### 5.1.2. Chemical Methods

Chemical methods can also be used to improve the quality of perovskite layers. The kinetics of generating nuclei and growing crystals are strongly affected by the chemical composition of the perovskite precursor solution. In particular, the surface morphology of perovskites is affected by their composition as well as by additives. Lee et al. reported that the addition of chloride ions to a perovskite precursor leads to improved smoothness of perovskite surfaces, enhanced grain sizes, and reduced concentration of pinholes.[72] In their experiment, mainly lead chloride (PbCl₂) was used as a chloride carrier. The addition of chlorides such as methylammonium chloride (MACl), ammonium chloride (NH₄Cl), or cesium chloride (CsCl) into a perovskite precursor solution leads to improved smoothness of perovskite surfaces, enhanced grain sizes and reduced concentration of pinholes.[71,73] The chloride anion is generally believed to favor the creation of perovskite nuclei by retarding the creation of lead iodide species, which are byproducts in fabricating perovskite crystals by competing with iodide ions in the complexation of Pb²⁺ ions.[74] In other words, additives containing chloride prevent crystallization processes forming pin or needle type crystals. The thin film, including the chloride ions, is converted into the perovskite, maintaining the existing homogeneous surface by passing through the intermediate states until reaching the final state.[75,76] The chloride ions can be removed by annealing as gaseous MACl. Due to these properties, chloride has been used in a variety of R2R compatible coating methods, including blading, slot-die coating, and spray coating.[32,59,75,77] In addition to the chlorides mentioned above, other organic halides or lead acetate (Pb(Ac)₂) were reported to form an intermediate state to obtain a homogeneous perovskite film.[78,79] Later, the formation of homogeneous perovskites by using hydrohalic acids as an additive instead of using antisolvent were reported.[80,81] These acids were claimed to have two effects: first, the acids provide anions that form intermediate species with Pb²⁺ to prevent crystallization of lead iodide, and second, they reduce the pH-value of the precursor, thereby influencing the rate of crystal production by destroying small crystals or nuclei of undesired byproducts.[81,82]

Many studies have also been performed from the point of view of Lewis acid–base interactions. In general, Pb²⁺ as a strong Lewis acid tends to combine with Lewis bases. This interaction improves the solubility of the lead halide in the precursor, thus slowing down the rate of nucleation and crystallization, which is favorable in terms of the LaMer concept. The rates of nucleation and crystallization are reduced with increasing concentration of the Lewis base and growing strength of its interaction with Pb²⁺. To observe this process, Lee et al. improved the quality of perovskite films by adding DMSO and thiourea as the Lewis bases.[83] Also N-cyclyl-2-pyrrolidone (CHP), hexamethylphosphoramide (HMPA), 1,8-diodooctane (DIO), and thio-semicarbazide (TSC) are Lewis bases and can be added into perovskite precursor solutions to improve the quality of perovskites, regardless of the coating technique applied.[81,84]

Another method suggested for modifying the quality of perovskite films consists in the regulation of the surface energy of the substrate before coating precursors. This method has been applied mainly to p-i-n perovskite solar cells, either by coating hydrophobic self-assembled monolayers (SAMs) on the substrate or adding nonpolar modifiers such as perylene into the HTL (PEDOT:PSS) to improve the
wettability of the substrate by the precursor. Also, the addition of polymers such as poly(vinylpyrrolidone) (PVP) to the precursor solution can improve the coverage of the substrate by perovskite and the smoothness of the final perovskite film. However, there are different opinions about this concept, e.g., Bi et al. argued that when the wettability is rather poor, the size of the perovskite crystals will be enhanced, due to the increased space available for individual crystals during crystallization.

5.2. Strategies for Upscaling Charge Extraction Layers

Charge transport layers also play a significant role in the upscaling of perovskite solar cells as they extract the photo-generated charges from the perovskite layer and thus influence the Voc of the cells. The charge transport materials should meet the following requirements for the upscaling of perovskite PV. First, they should have high charge carrier mobility and well-aligned energy levels for extracting the desired type of charge carrier from the perovskite active layer. Second, they should be low cost and easily deposited at low temperature to ensure low-cost large-scale PSCs manufacturing. Third, they should have good stability. In Figure 8b, some traditional HTL materials are shown. Spiro-OMeTAD is commonly used as the HTL material for giving high efficiency in large-area PSCs. However, only a few works have fabricated spiro-OMeTAD layers with R2R compatible techniques. In addition, two drawbacks have restricted the industrialization of spiro-MeOTAD. First, the cost of synthesis and purification of this material is around 500 $ g⁻¹. Second, the hole mobility of neat spiro-OMeTAD is only 5.3 × 10⁻⁵ cm² V⁻¹ s⁻¹, requiring dopants (lithium trifluoromethanesulfonimide, 4-tert-butylpyridine), which increase the hole mobility but at the same time reduce the PSCs lifetime. Therefore, other inorganic materials as well as organic small molecular and polymeric materials have been explored as alternatives to spiro-OMeTAD, but only a few materials are successfully applied in upsaling PSCs owing to their high cost, poor mobility, and low mobility. Using poly[bis(4-phenyl(2,5,6-trimethylphenyl)amine (PTAA) as HTL also exhibited PCE exceeding 20% but is not applicable for upsaling owing to its cost. Until now, concerning low cost and compatibility with R2R processes, NiOx, copper (I) thiocyanate (CuSCN), PEDOT:PSS, P3HT, and poly[2,2′′-bi[2-(butyloctyl)oxy]carbonyl][2,2′-5′,2′′-5″,2″′-quaterthiophene]-5,5″-diyl] (PDCBT) have the most promising perspective for large-scale PSCs manufacturing.

Electron transport materials are also quite important for upsaling perovskite solar cells. Low-temperature processable TiOx has been developed for flexible perovskite modules. Tin (IV) oxide (SnO2) is an attractive ETL material, which provides a higher open-circuit voltage, less hysteresis, and lower photocatalytic effect than TiOx. In addition, thin SnO2 films are claimed not to decrease the interconnection quality in a solar module, resulting in a low resistance ohmic contact between the front and the back electrodes. Zinc(II)oxide also exhibits PCE over 20% in PSCs but has been reported to show detrimental interactions with the perovskite layer, mainly in n-i-p devices. For p-i-n-type PSCs, fullerene derivatives (e.g., PC61BM, or SnO2/fullerene self-assembled monolayer (C60-SAM) are an option for upscaled manufacturing.

5.3. Strategies for Upscaling Electrodes

5.3.1. Bottom Electrode

The bottom electrode is essential to achieve high performance perovskite photovoltaics. Fluorine-doped tin oxide (FTO) and indium-doped tin oxide (ITO) are commonly recommended for PV because of their unique features including excellent conductivity, high transmittance, and good compatibility with the perovskite active layer. However, most of the devices for which record efficiencies have been reported were fabricated on those type electrodes on glass substrates, which are not applicable for the R2R upscaling process.

Especially for R2R compatible perovskite device architectures, the stability of the bottom electrode and the substrate is one of the key factors for a successful process. Generally, ITO-covered polymer substrates are selected as bottom electrodes because of their lower price, flexibility, transparency, and process stability. Most of the devices for which record efficiencies have been reported were fabricated on this type of substrates, such as ITO coated poly(ethylene terephthalate) (PET). However, deposition steps which require processing temperatures over 150 °C cause problems when working with polymer substrates. Park et al. have coped with this limitation by fabricating high-performance PSCs on colorless polyimide (CPI)/ITO substrate, which sustains a temperature of 300 °C during the fabrication process, with a PCE of 15.5%. To avoid the common problem of the temperature sensitivity of polymer substrates, some researchers tried to use metal foils as bottom substrates, which at the same time take over the role of the bottom electrode. In contrast to polymer substrates, metal substrates have high thermal stability, excellent barrier property, and high conductivity. However, as it cannot be used as a transparent substrate due to the opacity of metal, a transparent top electrode is essentially required. Troughton et al. addressed the deposition of perovskite on titanium (Ti)-foil and as the top electrode a (PEDOT:PSS)-covered nickel mesh was laminated onto the HTL. This work achieved 10.3% efficiency with excellent bending stability. Heo et al. suggested graphene layers as a top transparent electrode on perovskite fabricated on flexible Ti substrates, achieving a PCE of 15.0%. Recently, the copper foil has also been suggested as an alternative bottom electrode. Nejad et al. fabricated devices with the structure of Cu/CuI/MAPbI3/ZnO/AgNWs, showing a PCE of 12.8%.

In another direction for fabricating bottom electrodes, carbon-based materials are also applied because of their chemical stability toward perovskite. Qiu et al. deposited a perovskite layer on a multiwalled carbon nanotube (CNT) electrode, which was continuously intertwined with a fiber electrode. The fiber-shaped PSC achieved a PCE of 3.3% with good bending stability. PEDOT:PSS has been deposited on substrates as an electrode for flexible devices. Poorkazem et al. compared PSCs fabricated on two different transparent electrodes, PEDOT:PSS and ITO on PET substrates. It was reported that the PEDOT:PSS electrodes show better mechanical stability.
than ITO under periodical bending for 2000 cycles without any mechanical defects such as cracks, which in ITO-based perovskite devices result in extremely high sheet resistance and subsequent device performance degradation. Recently, on ITO coated Willow Glass of 100 µm in thickness, a gas quenching crystallized perovskite module with 15.86% on the 42.9 cm² aperture area was fabricated by Huang and co-workers. The Willow Glass can combine the advantages of glass substrates and good flexibility with the minimum bending radius of less than 100 mm (Figure 9).

5.3.2. Top Electrode

One of the main obstacles of the commercialization of perovskite PVs is the high price of the top electrodes made from gold and silver by vacuum evaporation. In addition, the metal electrode materials such as silver react easily with immigrated halogen atoms from perovskite, which directly deteriorates the photovoltaic performance. As an alternative, due to the low cost, high conductivity, and low processing temperature, carbon-based materials such as graphite/amorphous carbon, graphene, and CNTs have been addressed in the perovskite field. Another advantage of carbon-based material pertains to the reversible formation of the monohydrated phases CH₃NH₃PbI₃–H₂O and (CH₃NH₃)₄PbI₆–2H₂O, whereas with other electrode materials the dihydrate phase is formed, which degrades irreversibly to PbI₂ and MAI. Generally, carbon-based materials have a highly hydrophobic nature, which can lead to the prevention of moisture penetration toward the perovskite layer without any sealing process.

In 2018, De Rossi et al. addressed the first A4-size PSC having a carbon electrode, with an active area of 198 cm². In Figure 10, it is shown that most of the layers were fabricated by spray coating and screen printing. The active layer was fabricated by dripping precursor solution onto the porous carbon film. The perovskite module comprised 22 cells with dimensions of 5 × 180 mm² and interconnect spacings of 6 mm. With this large-area device, a PCE of 3.2% was reached. Recently, Yang et al. reported a processing protocol for highly efficient and stable planar n–i–p structure PSCs with carbon as the top electrode fully printed at fairly low temperature by using cheap materials under ambient conditions, thus meeting the requirements for scalable production on an industrial level. The optimized devices with all layers including SnO₂, perovskite, P3HT, and carbon electrode are printed under ambient conditions show efficiencies exceeding 18% with enhanced stability retaining 100% of its initial efficiency after 5000 h kept in the humid atmosphere. Further, large-area perovskite modules are successfully obtained and showed a PCE of 15.3%. These results represent carbon electrode perovskite devices as a promising approach for winning ingredient for the scaling up and worldwide diffusion of PSCs.

6. Module Design

The third challenge in upscaling PV technologies is how to make an economic module design for practical use. As with other thin-film PV technologies, it is not practical to fabricate a single PSC on a large-area substrate because the power loss due to the resistance of the transparent conducting electrode is substantial over a long transport distance. Resistance losses are reduced by dividing a large cell into smaller subcells with series interconnections to form a module. The series interconnections sum the voltages available from the subcells of the module. Some authors have also suggested connecting some of the cells in parallel, which leads to the summing up of the currents of the individual cells. The interconnections occupy ~1–20%
of the module area, depending on the geometry of the interconnection layout. The ratio between the photoactive area and the total area of a module is defined as the geometric fill factor (GFF) of the module. On one hand, the interconnection area is inactive for power generation and thus contributes linearly to the power loss in PV modules. On the other hand, the narrower the subcells, the lower the current, which reduces power losses quadratically with cell length. This leads to an optimum cell length, at which the power losses are minimized. The specific value depends on the current density provided by the respective material and can be calculated, e.g., by finite element modeling (Figure 11a).\textsuperscript{[118]} The simulations show clearly that at current densities of 20–25 mA cm\textsuperscript{−2}, power losses can be reduced to less than 10\% of the small cell values, but only, if cell lengths are reduced to 4 mm or less, if GFF exceeds 95\%, and if the sheet resistance of the transparent front electrode is less than 10 Ohms sq.\textsuperscript{−1}. The interconnect resistance itself has to be kept well below 0.01 Ohm cm\textsuperscript{−2}, i.e., care has to be taken that there is an excellent electrical contact between the bottom and top electrodes in this region.

A possible fabrication scheme for module assembly is to deposit each layer only at desired areas, thus requiring no postdeposition scribing to form the interconnections. Such on-demand deposition has been realized through patterned printing and deposition with masks. However, patterned deposition requires pattern alignment for each layer to be deposited, and the spatial resolution is typically low, with GFF not exceeding 80–90\%, thus causing large dead-area power losses.\textsuperscript{[119]}

The most convenient way of fabricating thin-film PV modules (CdTe, copper indium gallium diselenide (CIGS), organic solar cells (OSCs)) is generally by first depositing the thin-film materials homogeneously on the substrate and then separating individual cells by laser or mechanical scribing.\textsuperscript{[120]} This applies also to PSCs. There are three separation processes involved in module fabrication (Figure 11b). In the first step, the bottom conducting electrode (for example, transparent conductive oxide (TCO)) is divided into parts to form isolated substrates for the individual subcells; in the second step, the active material (ETL, perovskite, and HTL) is removed to construct interconnections between the subcells; the complete removal of the active layer, including charge extraction layers, without removing the bottom electrode, is essential for achieving low interconnect resistance. In the final step, the top electrodes and the edges of the module are isolated to separate the individual subcells and to define the outer boundaries of the module. Scribing with lasers is highly desirable for industrial production, with the advantages of low cost, fast production rate, and high GFF, which is associated with high precision and fine resolution.\textsuperscript{[104]} Perovskite modules fabricated through all-laser scribing have demonstrated a GFF of 94\%.\textsuperscript{[121]} Optimizing the subcell separation and module interconnection procedures for perovskite modules is important for scaling up PSCs and needs to be researched further. Recently, Poortmans and co-workers

---

Figure 10. a) Cross-section schematics of adjacent cells in the module produced by De Rossi et al., highlighting the laser-etched FTO, patterning of TiO\textsubscript{2} blocking layer, and the electrical vertical connection, ensured by the carbon back contact. b) Module layout. c) Photo of a module; wires have been soldered to the silver painted busbars. Reproduced with permission.\textsuperscript{[116]} Copyright 2018, Wiley-VCH.
reported a replacement of the line interconnections design with the point contact design can help decrease GFF losses. They designed that discontinuity in the P2 interconnection allows for the P3 interconnection line to meander around P2 points and to predominantly overlap with the P1 interconnection, decreasing the inactive area of the cell. As a result, perovskite modules fabricated through all-laser scribing have achieved a GFF of up to 99%.\cite{122}

7. Lifetime Aspects

Besides efficiency and cost, another important parameter to be considered is the lifetime of the solar modules as the outdoor service lifetime determines the overall energy generated by the module. The instability of perovskite devices is a serious obstacle for upscaling perovskite PV toward the market.\cite{121} As far as is known, the longest lifetime of perovskite solar cells is just one year;\cite{22} which is substantially shorter than the 25 years of commercial Si solar modules. Many factors affecting the lifetime of perovskite solar cells can generally be divided into two categories of external and intrinsic factors. External factors are moisture, oxygen, and UV light. When the perovskite materials are exposed to humid air, they decompose into mobile ions, mainly MA$^+$ and I$^-$, as well as insoluble PbI$_2$.\cite{124} The intrinsic factors are mainly thermal instability and ion migration. Degradation by external factors such as moisture, oxygen, and UV light can be reduced or eliminated by encapsulation. Encapsulation plays a key role in improving the durability of perovskite devices against harsh environmental conditions. Thin film encapsulation (TFE) with encapsulant between the substrate and the back cover is commonly used to seal PSCs. Glass-to-glass encapsulation is one of the most extensively used thin film encapsulation strategies. The encapsulant (e.g., ethylene vinyl acetate, polyurethane) is used to fill the package. And for the case of edge seal, epoxy resin and butyl rubber have been widely used as suitable encapsulant to prevent the moisture. In order to promote perovskite PV toward commercialization, more fundamental works need to be focused on exploring more suitable encapsulation materials and structures. The encapsulation materials with high transmittance, low Young’s modulus, low WVTR, and harmless byproducts are greatly needed.\cite{125} In addition, the material cost, processing cost, and processing time need to be took considered into the encapsulation solutions for commercial applications. The commercial UV-curing encapsulant, epoxy resin has higher WVTR and is more expensive than commonly used butyl rubber edge sealants. Glass frit is a novel edge sealing material, which can provide perfect moisture resistance, but it is quite expensive and is hardly commercialized. And combining the thin-film encapsulation and

---

Figure 11. a) Layout of a module consisting of three cells, with replacement circuit used for simulation. L: active cell length; l: patterning length; $R_{\text{top}}$ and $R_{\text{bottom}}$: series resistance of top and bottom electrodes, respectively; $R_{\text{int}}$: interconnect resistance. The photogenerated current is given with respect to the area of a single cell. P1 and P3: separation of bottom and top electrodes, respectively. P2: opening of active layer for the formation of contact between bottom and top electrodes of adjacent cells. b) Efficiency losses as a function of active cell length I) using $j_{\text{sc}}$ as parameter, II) active cell length using sheet resistance of the front electrode as parameter, III) interconnect resistance, and IV) active cell length using the patterning length $l$ as parameter. Reproduced with permission.\cite{119} Copyright 2015, Wiley-VCH. c) Top view and cross-section of a solar module with four cells connected in series with a magnified view of classical and point contact interconnections. Blue and red dotted lines indicate where the cross-sections are taken. Reproduced with permission.\cite{122} Copyright 2020, Wiley-VCH.
edge seal will be the future trend of the commercial encapsulation PSCs. Besides, upscaling encapsulation techniques such as flexible encapsulation should receive more attention from the community. As the back cover materials can meet the requirements of low-temperature process, high ductility and flexible material to be compatible with R2R fabrication process. The issue of thermal instability can be settled by tuning the perovskite composition to increase the decomposition barrier, for example, by increasing FA and guanidinium (GA) cations in the perovskite film.\textsuperscript{126} The ion migration problem can be solved by modifying the A site component with alkali ions (e.g., K\textsuperscript{+}, Rb\textsuperscript{+}).\textsuperscript{127} constructing a 2D perovskite to achieve multiple dimensional perovskite films, and by organic additives.\textsuperscript{128} Brabec and co-workers have shown that ion migration can also be eliminated by inserting a SAM layer of phosphonic acid derivatives of fullerene.\textsuperscript{129} In addition, the instability of perovskite solar cells may also be caused by the ETL. The commonly used TiO\textsubscript{2}-based ETL can induce photocatalytic degradation of the perovskite.\textsuperscript{130} Insertion of an interlayer between the TiO\textsubscript{2} layer (e.g., antimony sulfide,\textsuperscript{131} CsBr,\textsuperscript{132} SAM\textsuperscript{133}) or replacing TiO\textsubscript{2} with other UV stable materials (e.g., SnO\textsubscript{2},\textsuperscript{134} barium stannate (BaSnO\textsubscript{3}))\textsuperscript{135} could solve this problem. The most frequently used HTLs spiro-OMeTAD or PTAA also induce instabilities because of the mobility of their dopants (e.g., lithium salt, TBP).\textsuperscript{136} Inserting buffer layers (e.g., poly(methyl methacrylate) (PMMA)) between perovskite and the spiro-OMeTAD layer or replacing spiro-OMeTAD with undoped hole transport materials (e.g., P3HT, NiO\textsubscript{x}, CuSCN) can enhance device stability.\textsuperscript{137} The top electrodes such as gold, silver, and aluminum suffer from corrosion by ion migration in the perovskite layer, decreasing the lifetime of perovskite devices.\textsuperscript{138,139} In addition, when a perovskite device is exposed to light, migrating ions will gather at the interface, which will result in enhanced charge recombination. Aluminum electrode also suffer from instability due to humidity, as they can easily be oxidized in the humid air. Inserting an interlayer between the active layer and metal electrode (e.g., molybdenum oxide (MoO\textsubscript{3})\textsuperscript{140} tungsten oxide (Ta–WO\textsubscript{3})\textsuperscript{129} have been reported to hinder the diffusion of metals and ions and thus reduce deterioration.\textsuperscript{141} However, the better way is to replace them with stable electrode materials, e.g., by carbon, which is sufficiently inert and abundantly available at a low cost.\textsuperscript{139}

8. Summary and Outlook

The commercial success of perovskite PV as competitive technology to silicon depends mainly on the LCOE, i.e., on how well the parameters of the magic triangle of PV can be optimized. This implies that the costs of manufacturing perovskite PV well below 30 ct W\textsuperscript{-1} must be targeted to be competitive with Si PV. Direct competition with SiPV may be avoided by the development of alternative technologies, such as Si/perovskite tandem cells or the development of alternative applications, which are not amenable to Si, such as building integration or mobile applications.\textsuperscript{110}

Although a lot of effort has been invested into upscaling of perovskite PV technology, there is still a large gap between the efficiencies of small lab cells and large-area modules (Figure 1b). In addition, many of the hero module efficiencies have been achieved with materials, which are way too expensive for commercially viable solutions (Figure 1c). Thus, the successful way to commercialization requires further diligent optimization of both, materials and processes.

To make further progress toward the commercialization of perovskite PV, upscaling has to be optimized concerning the requirements of the magic triangle of cost, efficiency, and lifetime. Costs are determined by capex, throughput, and the bill of materials. To reduce manufacturing costs, establishing high throughput production without bottlenecks, including module patterning and encapsulation is essential. This may be realized through the highly automated S2S production (Figure 12a) or roll-to-roll production (Figure 12b). The latter ensures higher productivity at less capex, but requires flexible substrates and electrodes, which narrows down the range of acceptable materials. Vapor deposition steps should be avoided because they are costly, both with respect to capex and operation, and reduce throughput. Printing-based manufacturing requires further optimization of perovskite film crystallization, which requires rapid and controlled removal of solvent from large areas by appropriate quenching methods. For this purpose, gas quenching and high temperature deposition, also in combination, seem to be superior to solvent and vacuum quenching under the conditions of R2R processing. Employing efficient module layouts, optimizing subcell separation and interconnection procedures for perovskite modules is also considered a requirement for scaling up perovskite PV. The combination of full area coating, e.g., by slot die, and laser patterning seems to be most promising in this respect, but also restricts the

![Figure 12. Process flow of high throughput a) S2S and b) R2R production of perovskite modules. Reproduced with permission.\textsuperscript{149} Copyright 2017, Royal Society of Chemistry.](image-url)
choice of materials, especially for the top electrode, as will be pointed out later. It needs to be noted that only R2R production can deliver the desired throughput. Only inkjet printing and slot die can be easily integrated in a R2R production process. However, the slow printing speed inhibits the application on printing large-area PSCs. The viscosity of ink needs to be low enough to form droplets, which also is a limitation for its application in PSCs. The slot-die coating method could be the best option for upscaling perovskite solar cells as it has a low requirement for the materials and solution, can be easily assembled into R2R manufacturing. However, the lack of work in this area on slot-die coating perovskite film puts its performance behind the spin-coating counterparts. Therefore, more fundamental and comprehensive studies need to be conducted to explore the perovskite film formation mechanism of the slot-die coating method. Finally, affordable and fast in-line characterization of relevant parameters has to be developed to establish efficient quality control and maximize the production yield.

Under the aspect of the bill of materials, mainly the elimination or replacement of expensive materials for charge extraction layers and partially also for TCOs, without compromising lifetime and efficiency, is in the focus of future research. Concerning solution-processed HTLs, organic polymers like P3HT or PCBDT seem to be the most promising candidates for n–i–p architectures, while PEDOT:PSS or PTAA seems to be most appropriate for p–i–n architectures. Another cost aspect concerns the development of R2R compatible materials, i.e., materials that are appropriate for low-temperature processes, including the deposition of electrodes and electron extracting layers. Fabrication on PET substrates excludes sintering temperatures above 140 °C, while for polyimide, the acceptable temperature range extends to about 250 °C. Titania-based ETLs prepared from precursor solutions, as employed in nip devices, require high-temperature annealing and are thus not compatible with temperature-sensitive substrates. An alternative is the application of metal oxide nanoparticle layers, such as SnO2, which may be decorated with thin fullerene layers to reduce hysteresis. Another important aspect for R2R processes is the development of low-cost flexible substrates with perovskite compatible transparent electrodes, e.g., by introducing Ag diffusion barriers.[142] For printed top electrodes, carbon seems to be the most appropriate material, although laser patterning carbon paste is still a challenge due to the thick thickness of the carbon electrode (around hundred micrometers). Last but not least, avoiding hazardous materials is mandatory. Consequently, all printing processes have to be performed using “green” solvents. Finally, the concerns about lead introduce a factor of uncertainty in the efforts of commercialization. Although the amount of lead in perovskite modules is considered minute, there is certainly the need for further ecotoxicity/life cycle studies. Although there is vibrant research into potential replacements for lead, efficiencies are not yet impressive.[143] A promising way of accelerating the development of lead free materials systems may be the employment of automation and machine learning.[144] An alternative may be the development of low cost robust encapsulation for lead containment.

Table 2. The state art of power conversion efficiency versus lifetime. There are three aspects for improving the lifetime of PSCs, including interface engineering (interface), multidimensional perovskite (MDP), and inorganic cations doped in A site for ABX3 structure (doping). The hero lifetime of cells or modules is achieved by Nazeeruddin and co-workers based on the structure of FTO/compact TiO2/mesoporous TiO2/mesoporous ZrO2/2D–3D (HOOC(CH2)4NH3)2PbI4–CH3NH3PbI3/carbon showing zero efficiency loss over 10 000 h.[22]

| Device architecture | Area [cm²] | PCE [%] | Stability | Refs. |
|---------------------|-----------|---------|-----------|-------|
| FTO/c-TiO2/m-TiO2/m-ZrO2/2D–3D (HOOC(CH2)4NH3)2PbI4–CH3NH3PbI3/carbon | 47.6 (module) | 11.2 | >10 000 h zero loss | [22] |
| FTO/c-TiO2/m-TiO2/(FAPbI3)0.41(MAPbBr3)0.59/CuSCN/rGO/Au | 0.16 | 20.3 | Retain >95% of their initial efficiency after aging at a maximum power point for 1000 h under full solar intensity at 60 °C | [195] |
| FTO/c-TiO2/m-TiO2/RbCsMAFA perovskite/spiro-OMeTAD/Au | 0.1225 | 21.6 | Retain 95% of their initial performance at 85 °C for 500 h under full illumination and maximum power point tracking | [196] |
| FTO/PEDOT:PSS/(BA)2(MA)3PbI4/PC61BM/Au | 0.5 | 12.52 | Retain 65% under constant AM1.5G illumination over 2250 h | [197] |
| FTO/SnO2/PC61BM/Ba0.05(FA0.83Cs0.17)0.91PbI3/spiro-OMeTAD/Au | 0.0919 | 19.5 | Retain 80% under xenon-lamp simulated full-spectrum AM1.5, 76 mW cm−2 equivalent irradiance in air (humidity ≈45 RH%) without any ultraviolet filter over 1000 h | [198] |
| FTO/NiMg(Li)O/MAPbI3/PC61BM/Ti(Nb)Ox/Ag | 1.02 | 16.2 | With >90% of the initial PCE remaining after 1000 h of light soaking | [38] |
| ITO/C60-SAM/(FAPbI3)0.75(MAPbI3)0.25/PDCBT-Ta-WO3/Ag | 0.1 | 21.2 | 95% of its efficiency after 1000 h under 1-sun illumination | [96] |
| FTO/c-TiO2/m-TiO2/mesoporous ZrO2/ (S-AVA)2(MA)3PbI3/carbon | 0.07 | 12.8 | Stable for >1000 h in ambient air under full sunlight | [199] |
| FTO/c-TiO2/C2C8O2(FA0.83MA0.14PbI3.65Br0.35)/spiro-OMeTAD/Au | 1.1 | 19.3 | 95% continuous maximum power point (MPP) tracking for 500 h in nitrogen atmosphere under constant simulated solar illumination | [42] |
| ITO/SnO2–EDTAK/(BA)2(FA0.80Cs0.20)0.98PbI2.55Br0.45/EAI/spiro-OMeTAD/Au | 22.4 | 16.6 | Retained ≈86% of the initial performance after continuous operation for 2000 h under AM1.5G light illumination | [200] |
| FTO/NiO/(FA0.83MA0.17)0.95Cs0.05PbI3/spiro-OMeTAD/Au | 0.0919 | 19.8 | A degradation in performance of only around 5% for the encapsulated device under continuous simulated full spectrum sunlight for more than 1800 h at 70 to 75 °C | [201] |
question mark for the commercialization of this technology, due to its significant effect on LCOE, the lack of a broader data basis on lifetimes under operational conditions and the uncertainty about how well the devices showing hero lifetimes can be upscaled to large areas. The biggest challenge is certainly the development of a perovskite layer of high efficiency, which is at the same time stable against water, oxygen, illumination, and heat. Table 2 summarizes the state art of power conversion efficiency versus lifetime. Some mixed-cation perovskite based on Cs\textsubscript{x}FA\textsubscript{y}MA\textsubscript{1-x-y}PbI\textsubscript{3} have been reported recently as promising candidates, but there is certainly still a wide field of research opportunities. Passivation of interfaces, e.g., by small molecules, self-assembled monolayers, and low-dimensional perovskites materials, is another promising strategy for enhancing stability and performance at the same time. Another challenge is the replacement of spiro-OMeTAD, which on top of its tremendous cost, suffers from lacking stability. Candidates for printable, stable undoped HTLs are p-type semiconducting polymers, such as P3HT, PCDBT, and PTAA. Inorganic materials like NiO\textsubscript{x} and CuSCN are low-cost alternatives but suffer from inferior efficiency and processing issues. Generally, developing an ideal HTL should concern a suitable energy level, high mobility, and high transparency. Finally, inert top electrodes are required, which can be printed and are thus R2R compatible. Carbon pastes have demonstrated their potential for this purpose, but will need the development of high-resolution patterning methods to avoid a drastic drop in the geometric fill factor of perovskite modules.

A further challenge is the identification of affordable encapsulation materials, which provide sufficiently low values of water vapor transmission rates, the exact value depending on the stability of the perovskite layer against water and oxygen. The encapsulation processes must not only be R2R compatible but also compatible with the device materials. These comprise lamination of barrier films using UV curable adhesives or alternatively, the in-line deposition of diffusion barriers against water and oxygen, either by vacuum methods or by printing.

In conclusion, R2R-processed modules with efficiencies exceeding 15% and lifetimes of more than 20 years seem to be a realistic option in the near future. However, there is still ample room for the development of appropriate material systems, efficient module layouts, and robust processes with wide processing windows. Additionally, we need to address the magic triangle of photovoltaic key performance indicators (KPIs): efficiency, lifetime, and costs (of processing and materials). Figure 13b exhibits the suggested Stage-Gate process for the development of a perovskite device application. Depending on the stage of research, the level of technical complexity has to be increased, such as the transition from glovebox processing to air processing, from spin coating to a printing method, from cells to modules as well as from evaporated to printed top electrodes, which has to be considered for processing development.

Figure 13. a) Bill of materials calculated from the processes in spin-coating 1 cm\textsuperscript{2} perovskite solar cells. b) The suggested Stage-Gate process for the development of a perovskite device application. The gates have to be defined according to the application and should follow the critical key performance indicators (KPIs) for photovoltaics.
Between the individual research stages, performance-related gates control whether the material is mature enough to transit into the next stage. The gates need to monitor efficiency, lifetime, as well as the BOM of all layers (Figure 13a). This will prevent the progress of, e.g., expensive semiconductor or unstable interface materials to higher research stages. We strongly believe that this concept is applicable and beneficial to all emerging photovoltaic technologies that can rely on a broad and manifold material base, like organic, dye-sensitized, perovskite, or quantum dot technologies.

Acknowledgements

The authors acknowledge the “Solar Factory of the Future” as part of the Energy Campus Nuremberg (EnCN), which is supported by the Bavarian State Government (FKZ 20.2-3410.5-4-5), C.J.B. gratefully acknowledges the financial support through the “Aufbruch Bayern” initiative of the state of Bavaria, the Bavarian Initiative “Solar Technologies go Hybrid” (SolTech), and the SFB 953 (DFG, Project No. 182849149). F.Y. gratefully acknowledges the support by the National Natural Science Foundation of China (Grant No. 520021596) and Natural Science Foundation of Jiangsu Province (Grant No. BK20210731).

Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

high-efficiency, long-term stability, perovskite photovoltaics, roll-to-roll production, scalable coating

Received: June 28, 2021
Revised: September 13, 2021
Published online: October 8, 2021

[1] M. Cai, Y. Wu, H. Chen, X. Yang, Y. Qiang, L. Han, Adv. Sci. 2017, 4, 1600269.
[2] Z. Li, T. R. Klein, D. H. Kim, M. J. Yang, J. J. Berry, M. F. A. M. van Hest, K. Zhu, Nat. Rev. Mater. 2018, 3, 18017.
[3] D. B. Needleman, J. R. Poindexter, R. C. Kurchin, I. M. Peters, G. Wilson, T. Buonassisi, Energy Environ. Sci. 2016, 9, 2122.
[4] N. L. Chang, A. W. Y. Ho-Bailleau, P. A. Basore, T. L. Young, R. Evans, R. J. Egan, Prog. Photovolt: Res. Appl. 2017, 25, 390.
[5] C. Kost, T. Schlegl, J. Thomsen, S. Nold, J. Mayer, N. Hartmann, C. Senkpiel, S. Phillips, S. Lude, N. Saad, Levelized Cost of Electricity - Renewable Energy Technologies, Fraunhofer ISE, Freiburg, Germany 2018.
[6] F. Di Giacomo, A. Fakharuddin, R. Jose, T. M. Brown, Energy Environ. Sci. 2016, 9, 3007.
[7] A. Yang, M. J. Yang, D. T. Moore, Y. Yan, E. M. Miller, K. Zhu, M. C. Beard, Nat. Energy 2017, 2, 16207; b) D. H. Kim, J. B. Whitaker, Z. Li, M. F. A. M. van Hest, K. Zhu, Joule 2018, 2, 1437.
[8] T. Ibn-Mohammed, S. C. L. Koh, I. M. Reaney, A. Acquaye, G. Schileo, K. B. Mustapha, R. Greenough, Renewable Sustainable Energy Rev. 2017, 80, 1321.
[9] K. Bruening, B. J. Dou, J. Simonaitis, Y. Y. Lin, M. F. A. M. van Hest, C. J. Tassone, Joule 2018, 2, 2464.
Fu Yang received his Ph.D. degree under the supervision of Prof. Shuzi Hayase from Kyushu Institute of Technology, Japan, in 2019. After that, he worked as a postdoctoral researcher at Friedrich-Alexander Universität Erlangen-Nürnberg and a visiting scientist in the group of “Solar Factory of the Future” at ZAE Bayern in 2019–2021. He is currently an associate professor at the College of Chemistry, Chemical Engineering and Materials Science, Soochow University, in China. His research is focused on the scalable preparation and application of solution-printable photovoltaics.
Ning Li received his Ph.D. degree under the supervision of Prof. Christoph J. Brabec from Friedrich-Alexander Universität Erlangen-Nürnberg (FAU), Germany, in 2014. He is a research group leader at the Institute of Materials for Electronics and Energy Technology (i-MEET) and a visiting scientist at the Helmholtz Institute Erlangen-Nürnberg for Renewable Energy (HIERN) with research focus on the development and characterization of solution-processed materials and devices for photovoltaic applications, in particular on the aspects related to the industrialization of next-generation photovoltaics.

Christoph J. Brabec received his Ph.D. from Linz University, and joined the group of Alan Heeger at UC Santa Barbara for a sabbatical. He joined the SIEMENS (project leader) in 2001, Konarka in 2004 (CTO), Erlangen University (FAU–Professor) in 2009, ZAE Bayern e.V. (scientific director and board member) in 2010–2020, spokesmen of the Interdisciplinary Center for Nanostructured Films (IZNF) in 2013-2018, became an honorary professor at the University of Groningen and director at FZ Jülich (IEK-11) in 2018. His research interests include all aspects of solution processing semiconductor devices with a focus on photovoltaics and renewable energy systems.

Hans-Joachim Egelhaaf received his Ph.D. from Tübingen University for studying the photophysics of oligothiophenes. After habilitation, he moved to Politecnico di Milano to investigate organic semiconductors by ultrafast spectroscopy. In 2006, he joined Linz University to work with Konarka on organic solar cells. In 2009, he moved to Konarka in Nuremberg, where he became the director R&D after the acquisition by Belectric in 2012. Since 2014, he has been the head of ZAE Bayern’s “Solar Factory of the Future,” working on the upscaling of printed photovoltaics. He is also a lecturer at Erlangen University and the team leader at the Helmholtz Institute Erlangen-Nürnberg.