Solution processed perovskite incorporated tandem photovoltaics: developments, manufacturing, and challenges

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Abstract

Photovoltaics based on organic-inorganic as well as all inorganic semiconducting perovskites have emerged as a high performing concept at a lower cost. Intense research carried out in this regard over the last decade has resulted in single junction power conversion efficiencies that now exceed 25%. Furthermore, combining wide-bandgap perovskites in combination with other narrow-bandgap absorbers have enabled efficiencies exceeding 24% in combination with both perovskite as well as other narrow-bandgap absorbers such as silicon. Such tandem architectures provide the possibility of increasing power conversion efficiency with either a little increase in cost or even at a lower cost. In this review, we discuss emerging tandem concepts that incorporate perovskites in at least one sub-cell and can also be printed on roll-to-roll manufacturing lines. Initially, we discuss the progress in the field of perovskite/silicon tandem architectures followed by a discussion on perovskite/copper indium gallium selenide tandem devices. Then, recent progress in all-perovskite tandem devices is discussed. This is then followed by developments combining perovskites and organic bulk heterojunction absorbers. Subsequently, we discuss roll-to-roll and sheet-to-sheet printing techniques that can be used for scaled-up manufacturing of the above tandem concepts, which is then followed by reported work on perovskites that have utilised these printing techniques. Finally, we discuss prospects and future directions focusing on material stability and eliminating toxic solvents that are typically used in lab-scale perovskite solar cell fabrication processes and less well investigated applications such as for energy harvesting in space.

1. Introduction

Generation of energy through renewable sources and through sustainable means is one of the most important challenges humanity will have to overcome in the next few decades¹. Among the key technologies that can enable renewable energy generation, photovoltaic (PV) energy harvesting is gaining momentum as a major contributor. Currently, photovoltaic modules based on silicon stands by-and-far, the widely deployed PV technology. However, there is still the need towards developing PV technologies that enables high efficiencies at low increase in cost. Furthermore, technologies at lower costs compared to the current technologies with low specific power output² also open new market opportunities for non-grid based applications such as in building integrated photovoltaics³ etc.

Perovskite solar cells (PSCs), a thin film solar technology based on solution processable precursors, has rapidly emerged as both a competing, as well as supporting technology for Si PVs. Based on the ABX_3 formula (Fig. 1(a)), there have been a number of compositions for perovskites reported with the A-site consisting of either an organic cation such as methylammonium⁴ ($MA = CH_3NH_3^+$), formamidinium⁵ ($FA = CH(NH_2)_2^+$), or an inorganic cation such as cesium⁶ (Cs^+) or a combination of these^{7,8}, the B-site consisting of lead (Pb^{2+})⁷ or tin (Sn^{2+})⁹ or a mixture of these¹⁰⁻¹² and the X-site consisting of halides; iodide (I^-), bromide (Br^-), chloride (Cl^-)¹³ or a combination of these^{4,7,14}. Since its first demonstration as a photovoltaic material in 2009, the power conversion efficiency (PCE) of PSCs has seen a rapid increase from below 4%¹⁵ to 25.2%¹⁶. Such impressive performances have been enabled due to promising characteristics such as high optical absorption coefficients, long carrier diffusion lengths exceeding $1\ \mu m$ ¹⁷, excellent defect tolerance¹⁸ as well as low exciton binding energies¹⁹. Recent efforts have also seen developments in pathways for improved device stability^{20,21}. However, the performance of single junction PSCs are limited by the Shockley – Queisser limit of $\sim 33\%$ ²². A potential route towards bypassing this limit is through the formation of tandem architectures which is enabled by the bandgap (E_G) tunability²³ of perovskite absorbers through compositional engineering of the halides¹⁴, or the B-site¹² enabling the formation of both wide bandgap and narrow bandgap absorber fabrication (Fig. 1(b) and (c)). This in turn has resulted in impressive developments not only in perovskite/Si tandem architectures with PCEs exceeding 29% (certified)¹⁶, other perovskite incorporated tandem devices with efficiencies approaching 25%^{12,16,24}.

As highlighted above, one of the key attractions of PSCs has been their solution processability. This can potentially enable high-throughput production based on roll-to-roll (R2R) and sheet-to-sheet (S2S) fabrication methodologies based low cost, high throughput printing techniques such as slot die coating, ink jet printing, spray coating, doctor blading. In fact, there are ongoing industrially driven research and development activities towards the realization of printed perovskite solar technologies from companies such as Panasonic²⁵, Saule Technologies²⁶, and more recently, Swift Solar²⁷ to name a few.

With the developments in large area printed single junction perovskites, it is timely and important to consider the possibility of incorporation of such printed perovskite layers to manufacture tandem architectures. While the tandem device architectures can result in an increase in cost, this is often argued to be offset by the potentially higher PCEs possible. In fact, the possibility of developing low cost tandem architectures based on printed technologies was a key goal for organic photovoltaic (OPV) technologies towards realizing low cost renewable energy generation.^{28,29} With the advent of perovskites it is evident that the possibilities for such all printed tandem technologies have also dramatically enhanced. Some of the possible combinations in this regards include PSC (wide E_G)/silicon (narrow E_G) or PSC (wide E_G)/copper indium gallium selenide (CIGS, narrow E_G) for semi-printable approaches or PSC (wide E_G)/PSC (narrow E_G) or PSC(wide E_G)/OPV (low E_G) or even organic photovoltaics (OPV, wide E_G)/PSC (low E_G) combinations for all-printed approached.

This review is structured as follows (Fig. 1(d)): initially, we will discuss the benefits of tandem architectures. This will be followed by developments in perovskite incorporated 2-terminal (2T) tandem technologies. Initially, we discuss recent developments in perovskite/silicon and perovskite CIGS tandem devices. This is followed by a discussion on potentially all-solution processable 2T which includes all-perovskite tandem architectures, perovskite-OPV tandem architectures and, other emerging systems such as those based on quantum dots. We then discuss developments made in R2R and S2S printing techniques for printing perovskite absorbers. Finally, we outline the current challenges and future directions that can enable such printed, perovskite incorporated tandem architectures to be realized.

Fig. 1 (a) The arrangement of ions under the ABX_3 crystal structure for a perovskite. (b) Example of bandgap tunability of perovskites.³⁰ Here the X-site (Cl^- , Br^- , I^-) composition is varied in CsPbX_3 quantum dots. Reprinted with permission from Ref. 30. Copyright (2015) American Chemical Society. (c) Bandgap tunability of perovskites shown here through variation of the B-site and X-site.²³ Reproduced from Ref. 23 with permission from Wiley-VCH. (d) The overall structure of this review discussing the material combinations, printing methods and challenges, prospects.

2. 2T tandem technologies

One of the principle bottle necks of a single junction technology is the thermalization losses³¹ ((Fig. 2(a)) due to the absorption of photons with energies higher than the E_G , which restricts the maximum possible cell voltage to $(E_G - 0.3)/e$ V where e is the electronic charge and the 0.3 eV term is due to fundamental thermodynamic losses^{32,33}. One potential route towards bypassing this limit is thorough combining sub-cells in a series connection³¹ (Fig. 2(b)) where the photocurrent generated in each cell is matched or balanced to minimize losses. This has in fact resulted in III-V multijunction cells consisting of six junctions with PCEs exceeding 39%¹⁶.

The theoretical maximum for all PV devices is estimated based on the detailed balance limit principle³². For single junction devices, this often results in a theoretically possible maximum of 33% for a single junction cell which is increased to ~46% for a 2T 2-junction (2J) (Fig. 2(c)) architecture. This can be further increased up to 52% for a triple junction (3J) architecture, and up to 68% for an infinite number of junctions³⁴. With regards to perovskites incorporated in tandem architectures, Hörantner et al.³⁵ estimated the impact of fabrication of all perovskite tandem architectures based on 2T-2J concept by combining absorbers with E_G s of 0.9 – 1.35 eV & 1.5 – 2.0 eV which was shown to enable PCEs of ~32% while a 2T-3J scheme combining sub-cells with E_G of 1.22 eV, 1.50 – 1.90 eV & 1.90 – 2.30 eV was shown to enable PCEs of 33.1% (Fig. 2(e)-(f)). It was noted that the appropriate matching of E_{BGs} is crucial in obtaining the best PCE. In terms of combining perovskites with absorbers based on other semiconductors (e.g. OPVs), it is noted that appropriate losses that are over and above the losses typically observed for crystalline systems should also be also taken into consideration. For example, in OPVs, the fundamental voltage loss for a large portion of its early development was identified to be at 0.6 V due to the energy level alignments required for exciton dissociation. However with the recent resurgence in the field in development of new donor and acceptor systems, this loss has been reduced³⁶, thereby enabling the previously identified target of 15%²⁹ for 2T-2J architecture to be surpassed³⁷.

Beyond the benefit of minimizing thermalization losses, the use of multijunction concepts can also enable the balancing of optical absorption with efficient charge extraction. For example, while increasing the thickness of an absorber is beneficial to enable a higher generation of carriers, this may not be matched with the diffusion lengths of the absorber material. Therefore, the stacking of the same absorber to form multijunction architectures is also seen as a favorable

route towards minimizing losses³⁸. This has been implemented in both OPVs and as well as in all-perovskite architectures.

Fig. 2 Contribution of different loss mechanisms under (a) varying absorber E_g and (b) number of junctions in a tandem architecture.³¹ Reproduced from Ref. 31 with permission from Wiley-VCH. (c) The predicted theoretically possible PCE for different combinations of top and bottom cell bandgaps.³⁴ The white circle indicates the maximum PCE. Reproduced from Ref. 34 with permission from Springer Nature. (d) Potential multijunction cell combinations whose estimated PCEs are given in (e) for 2T-2J tandems combining absorbers with E_g s of 0.9 – 1.35 eV & 1.5 – 2.0 eV, (f) for 2T-3J devices with absorber E_g of 1.22 eV combined with 2 absorbers possessing E_g in the 1.50 – 1.90 eV range & (g) for absorber E_g of 1.22 eV combined with 2 absorbers possessing 1.90 – 2.30 eV.³⁵ Reprinted with permission from Ref 35. Copyright (2017) American Chemical Society.

3. Perovskite incorporated tandem concepts

We now proceed to discuss tandem technologies that have been reported based on the incorporation of a perovskite absorber.

a) Perovskite/silicon tandem photovoltaics

From the photovoltaic technologies that have been studied and developed so far, crystalline silicon (c-Si) has been the most successful in terms of commercial implementation. Consisting of a low E_G of 1.1 eV, high PCEs exceeding 23% over large areas, non-toxicity and excellent stability, c-Si has been the benchmark for all emerging single junction PV technologies.¹⁶ As the efficiency of single junction cells approaches the theoretical limit for this material³⁹, there have been significant efforts to identify an appropriate wide E_G absorber to form tandem architectures. Among the technologies that enable the formation of wide E_G sub-cells, perovskites have so far been the most promising due the bandgap tunability over 1.6 – 1.8 eV through compositional engineering, low processing costs, and high efficiency.^{40,41} As a result, an industrial demonstrator with a PCE of 28% based on a 2T perovskite/silicon tandem cell has been reported by Oxford PV which was recently exceeded by a 2T perovskite/silicon architecture with a PCE of 29.2%.¹⁶ The latter is the first demonstrator where the efficiency of a single junction c-Si cell has been exceeded based on the incorporation of a printable wide E_G cell. In terms of the c-Si cell, both homojunction and heterojunction architectures have been used in conjunction with a perovskite sub-cell. Si heterojunction technology (SHT) offers improved device performance and cost advantages,⁴² although the former, which accounts for >80% of the market share for photovoltaics⁴³ enables processing at higher temperatures, enabling compatibility with the mesoporous perovskite architecture⁴⁴. In the following sections, we will first discuss developments based on homojunction Si technologies followed by developments using SHT. A summary of reported device performances is given in [Table 1](#).

The first reported work on a 2T perovskite/silicon based on a silicon homojunction architecture was by Maillat et al.⁴⁵ The perovskite absorber used was based on the MAPbI₃ composition which was identified to possess an E_G of 1.61 eV. Utilizing a mesoscopic architecture for the perovskite cell in combination with a c-Si cell resulted in a PCE of 13.7%. The low PCE observed were attributed to several issues including the use of a non-textured surface for fabrication of the perovskite sub-cell and lack of passivation. Indeed, the use of non-textured surface has been a favoured approach for a majority of developments in perovskite/silicon tandem architectures due to difficulties in achieving conformable perovskite coatings on

textured surfaces. However, we note recent reports that identify routes towards the deposition of perovskites on textured surfaces.^{46,47} Following the above work, Werner et al. reported⁴⁸ a tandem architecture comprising of a high temperature processed mesoscopic perovskite sub-cell together with a c-Si cell. A PCE of 16% was achieved, which is higher than that reported by Mailoa et al.⁴⁵ This was enabled by incorporation of passivation strategies for the silicon sub-cell and also the use of better optimized recombination layers. Silicon oxide (SiO_x) was used as a passivation layer on both surfaces of the *n*-type silicon wafer which enabled a higher V_{OC} to be achieved compared to Mailoa et al.⁴⁵ The hole-collecting emitter (through boron implantation), as well as the local contact and back surface field (BFS) formation (through phosphorous implantation) was formed through laser patterning. Improvements in PCE were also driven by optimization of the recombination layer thicknesses. This was also noted to influence the optical interference pattern in the Si cell which occurs due to the refractive index mismatch between compact titanium oxide (c- TiO_2) electron transport layer in the perovskite sub-cell and the zinc tin oxide (ZTO) recombination layer. As noted above, the optimization of the optical coupling due to the influence of each layer used in tandem architectures is another key point for PCE gains. Further improvements in the PCE for the above work was noted to be limited by the interfacial resistance which limited the fill factor (*FF*) of the device. A significant improvement for perovskite/silicon tandems incorporating a mesoscopic perovskite sub-cell was reported by Wu et al.⁴⁹ where a PCE of 22.5% was obtained. The authors incorporated several notable improvements. Firstly, passivation of front and rear surface was carried out which also enabled optimization of the optical coupling. An alumina (Al_2O_3)/silicon nitride (SiN_x) bilayer was used on the front surface for better matching of refractive indices and suppression of reflection losses while the rear SiN_x layer enhanced light trapping (and as a result, the current). To minimize resistive losses due to the contact resistance between the indium tin oxide (ITO) recombination layer and the boron emitter, a factor which restricted the performance in the cells developed by Werner et al.⁴⁸, an array of Cr/Pd/Ag metal stacks was used for the contact openings. The authors also used a quadruple cation composition⁵⁰ of the form $\text{Cs}_{0.07}\text{Rb}_{0.03}\text{FA}_{0.765}\text{MA}_{0.135}\text{PbI}_{2.55}\text{Br}_{0.45}$ which when processed with vacuum flash assisted solution process (VASP) as reported by Bi et al.⁵¹ improved reproducibility.

In most of the above reports, the use of a relatively high conductivity metal oxide recombination contact has been a common factor. Zheng et al.⁵² demonstrated a tandem device based on a planer MAPbI_3 cell where such a recombination contact was removed. The resulting

devices demonstrated steady-state PCEs of 20.5% over 4 cm² and 17.1% over 16 cm². In place of the widely used TiO₂ electron extraction contact for the perovskite, tin oxide (SnO₂) based on a colloidal solution was used, enabling compatibility with printed manufacturing routes. Rear texturing of bottom silicon cell enabled improved light trapping while the use of a metal grid together with the top ITO transparent contact also minimized sheet resistance losses, thereby improving device *FF*. Shen et al.⁴³ developed a similar concept where c-TiO₂ deposited using atomic layer deposition (ALD) on both homojunction as well as passivating contact heterojunction cells. Together with a Cs_{0.05}Rb_{0.05}FA_{0.765}MA_{0.135}PbI_{2.55}Br_{0.45} leading to stabilised PCEs of 22.8% and 24.1% respectively (Fig. 3(a) and (b)).

One of the limitations perovskite incorporated tandem architectures has been the parasitic absorption losses due to 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro-OMeTAD), the most widely used hole transport layer in PSCs. To mitigate this issue, Zheng et al.⁵³ used textured polydimethylsiloxane (PDMS) film that incorporated a down-shifting phosphor (Ba,Sr)₂SiO₄:Eu²⁺ in front of monolithic perovskite/silicon tandem. The phosphor converted near UV light to visible light, thereby bypassing parasitic absorption losses in Spiro-OMeTAD. Based on the above approach, a further improved PCE of 23.1% on 4 cm² cell with a high *FF* of 81% was reported (Fig. 3(c)).

In the above reports, *n*-type silicon was widely adopted. However, *c*-Si cells based on *p*-type Si account for a large market share.⁵⁴ Therefore, in this regard, it would be advantageous to develop perovskite/silicon tandem architectures based on *p*-type Si wafers. In this regard, Kim et al.⁵⁵ reported design rules for planar monolithic perovskite/*p*-type Si Tandem solar cells based on controlling of the thickness and *E_G* of the perovskite absorber as well as the selection of an appropriate hole transport layer. Using a double cation (FAPbI₃)_{0.8}(MAPbBr₃)_{0.2} composition, a PCE of 21.19% was achieved.

The first perovskite/silicon tandem architecture based on the SHT concept was reported in 2015 by Albrecht et al.⁵⁶. The authors reported the use of atomic layer deposited SnO₂ to form the electron extraction contact, enabling a stabilized PCE of 18.1% to be achieved together with high *V_{OC}* of 1.78 V. The use of ALD for the SnO₂ continues to be the preferred route for the formation of a metal oxide electron extraction layer in a majority of perovskite based tandem cells to-date. Almost immediately following the above work, Werner et al.⁵⁷ reported a perovskite/silicon tandem cell with an improved PCE in excess of 21%. The most notable feature of the work was the incorporation of an indium zinc oxide (IZO) window as the

recombination layer together with solution processed polyethyleneimine (ethoxylated) (PEIE)/phenyl-C61-butyric-acid-methyl-ester (PC₆₁BM) bilayer for electron extraction from the perovskite sub-cell which facilitates low temperature processing. The authors also employed a two-step fabrication process for the MAPbI₃ perovskite absorber with MAI being solution deposited on thermally evaporated PbI₂, a route that shows promise for perovskite deposition on textured surfaces.⁴⁶ Through optimization of the IZO thickness, they achieved a stable PCE of 21.2% over an aperture area of 0.17 cm² and 19.2% over an aperture area of 1.22 cm². One of the key issues in the above work by Werner et al.⁵⁷ was the limited near infrared response of the Si sub-cell due to the non-textured cell used. This was reduced in a subsequent study by Werner et al.⁵⁸ where a PCE of 20.5% was reported for an area of 1.43 cm². The rear-side texturing on the bottom cell led to an enhancement of the photocurrent response of the Si sub-cell in the near-infrared region. Zhue et al.⁵⁹ demonstrated the possibility of obtaining high efficiencies following careful optimization of the top MoO₃ buffer layer and ITO transparent electrode stack. Through careful tuning of the thickness and the deposition conditions to reduce optical and electrical losses, they achieved a further improved PCE of 22.8%.

While most of the above reports for SHT based work used MAPbI₃ as the absorber, this has a lower E_G than is typically desired for tandem architectures. Based on this, Fan et al.⁶⁰ investigated the impact of E_G tuning in mixed A-site cation compositions by the use of mixed halides (iodine and bromine). In their work, MA_{0.37}FA_{0.48}Cs_{0.15}PbI_{2.01}Br_{0.99} with an E_G of 1.69 eV was identified to be optimum. they fabricated monolithic perovskite tandem solar cell with the steady state PCE of 18%. Qiu et al.⁶¹ followed a similar approach and identified MA_{0.38}FA_{0.50}Cs_{0.12}PbI_{2.04}Br_{0.96} as possessing the optimum E_G of 1.69 eV for perovskite/silicon tandem solar cells. Through further optimization of the SnO₂ electron transport layer thickness, the authors achieved a steady state PCE of 20.6%, similar to Fan et al.⁶⁰

One of the key concerns in the above perovskite compositions has been the use of methylammonium which typically regarded to introduce device instabilities under heating.⁶² This has led to the development of compositions consisting Cs and FA.^{8,14} Based on this, Bush et al.⁶³ developed Cs_{0.17}FA_{0.83}PbI_{0.83}Br_{0.17} based perovskite/silicon tandem cells with a PCE of 23.6% over 1 cm² featuring rear textured SHJ. A SnO₂/ZTO deposited using ALD/pulsed-chemical vapour deposition enabled a hole blocking window layer with lower parasitic absorption. The photocurrent losses in the infrared region was reduced by using a Si nanoparticle incorporated rear reflector which allowed appropriate refractive index matching. Bush et al.⁶⁴ later reported further improvements in PCE through reduction of the optical losses

that was present in their previous work.⁶³ This was achieved by optimizing the perovskite composition to achieve a wider E_G , reducing front reflection losses by thinning of the ITO electrode and introduction of metal fingers to minimize sheet resistance losses due to the thinner ITO layer, and the incorporation of a polydimethylsiloxane (PDMS) stamp with random, pyramidal texture to further reduce front side reflection losses. They achieved 25% efficiency on a 1 cm² cell.

In addition to its use in the rear electrode, nanocrystalline Si (nc-Si) has also been used in the recombination layer. For example, Sahli et al.⁶⁵ who utilized a hydrogenated nanocrystalline Si (nc-Si:H) layer, deposited by plasma-enhanced chemical vapor deposition (PECVD) at low temperature, as recombination junction. This led to a decrease in the parasitic absorption and reflection losses leading to PCEs of 22%, 21.2% and 18% for active areas of 0.25, 1.43 and 12.96 cm². Sahli et al.⁴⁶ used a similar concept on the first perovskite/silicon tandem architecture where the perovskite was deposited on a textured silicon bottom cell (Fig. 3(d) – (f)). For this purpose, a hybrid two-step deposition method combining sequential co-evaporation of PbI₂ and CsBr₂ and spin coating of FABr and FAI mixture to form the conformal perovskite absorber layer. A certified steady-state PCE of 25.2% over an aperture area of 1.419 cm² was achieved based on the above architecture and processing. Nogay et al.⁵⁴ adopted a similar approach with a *p*-type, textured Si based bottom cell by where a steady-state PCE of 25.1% and a reverse scan PCE of 25.4% was achieved for devices with an active area of 1.42 cm².

Other than nanocrystalline Si layers, optimized hydrogenated nanocrystalline silicon oxide (nc-SiO_x:H) layers⁶⁶ have also been reported as a suitable interlayer. Ren et al.⁶⁷ improved the near infrared response of SHJ solar cells by using wide band gap and low refractive index hydrogenated nanocrystalline silicon oxide (nc-SiO_x:H) layer on a smooth c-Si wafer together with an *n*-type back surface field (BSF) layer resulting in a PCE of 20.1%. Mazzarella et al.⁶⁸ also reported monolithic perovskite/silicon cell which employed a nc-SiO_x:H as the interlayer between the silicon and perovskite sub-cells. An increased bottom cell current density due to reduction in reflection losses as a result of the nc-SiO_x:H enabled a certified PCE of 25.2% (stabilized). The use of nc-SiO_x:H together with the incorporation of a textured light management (LM) foil on the front-side of a tandem solar cell processed on a planar front-side wafer consisting of and textured back-side was reported by Jošt et al.⁶⁹ The resulting improvement in optical management led to an increase in PCE from 23.4% to 25.5% for tandems consisting of perovskites with Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}Pb_{1.1}(I_{0.83}Br_{0.17})₃. Hou et al.⁷⁰

utilized a nc-SiO_x:H layer which together with a PDMS as an antireflective foil resulted in improvement in PCE from 19.38% to 21.93%.

Processing of the perovskite layer is another key aspect that drives high performing perovskite/silicon tandem PVs. Zhu et al.⁷¹ reported the importance of optimization of dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) as means of optimizing the properties of the perovskite layer, which in turn impacts the light absorption and transmission within a tandem device structure. This approach was demonstrated for both FACs based and FAMACs based perovskite compositions, with the latter resulting in a PCE of 22.8%. Other than solvent engineering, the incorporation of additives is now rapidly becoming a preferred approach towards grain engineering and modification of morphology in perovskite absorbers. For example, Chen et al.⁷² incorporated methyl ammonium chloride (MACl) and MAH₂PO₂ into the perovskite precursor. These additives were shown to modify the crystallization process, resulting in PCE of 25.4% for perovskite/silicon tandem devices. More recently, Xu et al.¹³ reported the incorporation of chlorine into a FACs based perovskite composition as means maintaining an E_G of 1.67 eV (suitable for tandem architectures), while reducing the bromine content. While high bromine loadings enable wider bandgaps to be achieved, this often results in light induced halide segregation⁷³, leading to solar cell performance drift. Based on the above approach, the authors reported an impressive PCE of 27% efficiency over 1 cm². However, it is noted that the excess chloride was added to the perovskite precursor in the form of MAPbCl₃ and as of present, the role of the excess MA on the above device characteristics remains unclear. Mitigation of halide segregation has also been reported to be possible through solvent post-treatment. For example, Hou et al.⁴⁷ reported a PCE of 25.7% efficiency via post treatment of the perovskite film with 1-butanethiol (Fig. 3(g) and (i)). The resulting self-limiting passivation layer formed on rough and micrometer thick perovskite surfaces was reported to increase carrier diffusion length while mitigating phase segregation. More importantly, this work also reported the first example of an entirely solution processed perovskite layer on a textured Si surface (Fig. 3(h)). The shunting of devices which is usually anticipated when solution processed layers are deposited on textured surfaces with high peak-to-trough dimensions was avoided through the use of thick perovskite layers. Approaches to passivate of grain boundary recombination in tandem solar cells have also followed trends utilized in perovskite single junction cells. In this regard, Kim et al.⁷⁴ reported the grain boundary passivation of a 1.68 eV perovskite absorber through the incorporation of phenethylammonium (PEA)-based two-

dimensional (2D) additives together with a thiocyanate (SCN) which enabled a PCE of 26.7% to be achieved (Fig. 3 (j) – (m)).

Fig. 3 (a) Schematic of the device architecture and (b) *J-V* characteristics of perovskite/silicon tandem cell that utilizes an in-situ built recombination layer.⁴³ Reproduced from Ref. 43 under the Creative Commons Attribution Non-Commercial License 4.0 (CC BY-NC). (c) The *J-V* characteristics of 4 cm² perovskite/silicon tandem PV as reported by Zheng et al.⁵³ incorporating the down-shifting phosphor (Ba,Sr)₂SiO₄:Eu²⁺ within a PDMS antireflection layer. Reprinted with permission from Ref 53. Copyright (2017) American Chemical Society. (d) Schematic of device architecture of the first reported perovskite/tandem architecture where the perovskite is deposited on a textured surface through combined thermal evaporation and spin-coating process, (e) cross sectional EDX image indicating accumulation of Spiro-TTB on an ITO recombination junction (when annealed) as opposed to a more uniform coating when deposited on nc-Si:H, and (d) the *J-V* characteristics for the certified device.⁴⁶ Reproduced from Ref. 46 with permission from Springer Nature. (g) Device schematic, (h) *J-V* characteristics for the certified device and (i) cross sectional image of perovskite/silicon tandem device where the perovskite was solution processed on a textured silicon surface.⁴⁷ From Ref. 47. Reprinted with permission from AAAS. (j) and (k) TEM images indicating the formatting of a 2D phase at the grain boundary for PEA(I_{0.25}SCN_{0.75}) incorporated perovskites as reported by Kim et al.⁷⁴ The inset in (k) shows the fast Fourier Transform pattern of the 2D perovskite. (l) Cross sectional image and (m) *J-V* characteristics of perovskite/silicon tandem devices from Ref. 74. From Ref. 74. Reprinted with permission from AAAS.

Table 1. Summary of performance characteristics for perovskite/silicon tandem photovoltaics. SPO indicates stabilised power output. Note: *Mask area > active area

Year	Configuration	V_{oc} (V)	J_{sc} (mAcm^{-2})	FF	PCE (%) (SPO(%))	Ref
2015	Metal/ n^{++} Si BSF/ n -type Si (Base)/ p^{++} Si (Emitter)/ n^{++} Si TJ/c-TiO ₂ /mp-TiO ₂ /MAPbI ₃ /Spiro-OMeTAD/Ag NW/LiF	1.58	11.5	75	- (13.7)	45
2015	Ag/AZO/a-Si:H (n^+)/a-Si:H (i)/ n -type Si/a-Si:H (i)/a-Si:H (p^+)/ITO/SnO ₂ /((FAPbI ₃) _{0.85} (MAPbBr ₃) _{0.15} / Spiro-OMeTAD/MoO ₃ /ITO/LiF	1.785	14	77.3	19.1 (18.1)	56
2015	Ag/ITO/a-Si (n)/a-Si (i)/ n -type Si/a-Si (i)/a-Si (p)/IZO/PC ₆₁ BM/PEIE/MAPbI ₃ /Spiro-OMeTAD/MoO ₃ /ITO/IO:H	1.692	15.8	79.9	21.4 (21.2)	57
2016	Al/BSF/ n -type Si (Base)/ p^{++} Si (Emitter)/ZTO/ c-TiO ₂ /mp-TiO ₂ /MAPbI ₃ /Spiro-OMeTAD/MoO _x /IO:H/ITO	1.643	15.3	64.8	16.3 (16)	48
2016	Ag/ITO/a-Si (n)/a-Si (i)/ n -type Si/a-Si (i)/a-Si (p)/IZO/PC ₆₁ BM/PEIE/MAPbI ₃ /Spiro-OMeTAD/MoO ₃ /ITO/IO:H	1.717	16.4	73.1	20.6 (20.5)	58
2017	Ag/Al/ n^+ Si/ n -type Si/ p^+ Si/Cr/Pd/Ag/ITO/ c-TiO ₂ /mp-TiO ₂ /Cs _{0.07} Rb _{0.03} FA _{0.765} MA _{0.135} PbI _{2.55} Br _{0.45} /Spiro-OMeTAD/MoO _x /IZO	1.75	17.6	73.8	22.8 (22.5)	49
2017	Al/ITO/a-Si (n)/a-Si (i)/ n -type Si/a-Si (i)/a-Si (p)/ITO/SnO ₂ /MAPbI ₃ /Spiro-OMeTAD/MoO ₃ /ITO	1.687	15.62	68	18 (-)	59
2017	Ag/a-Si (n^+)/ n -type Si/a-Si (p^+)/ITO/SnO ₂ /MA _{0.37} FA _{0.48} Cs _{0.15} PbI _{2.01} Br _{0.99} /Spiro-OMeTAD/MoO _x /ITO	1.703	15.25	79.22	20.57 (18)	60
2017	Ag/Si NP/ITO/a-Si (p^+)/a-Si (i)/ n -type Si/a-Si (i)/a-Si (n^+)/ITO/NiO/FA _{0.83} Cs _{0.17} Pb(I _{0.83} Br _{0.17})/LiF/PC ₆₁ BM/SnO ₂ /ZTO/ITO/LiF	1.65	18.1	79	23.6 (23.6)	63
2017	Ag/TCO/a-Si:H (n^+)/a-Si:H (i)/ n -type Si/a-Si:H (i)/a-Si:H (p^+)/nc-Si (p^+)/ nc-Si (n^+)/ C ₆₀ /Cs _{0.19} FA _{0.81} PbI ₃ / Spiro-OMeTAD/MoO ₃ /IZO/MgF ₂	1.751	16.8	77.5	22.8 (22)	65
2018	Ti/Pd/Ag/ n^{++} Si/ n -type Si/ p^{++} Si (Emitter)/SnO ₂ /MAPbI ₃ /Spiro-OMeTAD/MoO ₃ /ITO/Ag busbar/PDMS AR foil	1.676	16.1	78	21 (20.5)	52
2018	Ag/a-Si (n)/a-Si (i)/ n -type Si/a-Si (i)/a-Si (p)/IZO/PC ₆₁ BM/PEIE/MAPbI ₃ /Spiro-OMeTAD/MoO ₃ /ITO/	1.655	16.5	81.1	22.22 (20.6)	61
2018	Ag/ITO/a-Si (p^+)/a-Si (i)/ n -type Si/a-Si (i)/a-Si (n^+)/ITO/PTAA/FA _{0.75} Cs _{0.25} Pb(I _{0.8} Br _{0.2}) ₃ /LiF/C ₆₀ /SnO ₂ /ITO/PDMS	1.77	18.4	77	25 (-)	64
2018	Al/ITO/nc-SiO _x (n)/a-Si:H (i)/ n -type Si/a-Si:H (i)/nc-SiO _x (p)/ITO/SnO ₂ / MA _{0.70} FA _{0.23} Cs _{0.07} PbI _{2.25} Br _{0.75} /Spiro-OMeTAD/MoO _x /ITO/PDMS	1.75	16.89	74.18	21.93 (-)	70
2018	Ag/ITO/a-Si (p)/a-Si (i)/ n -type Si /a-Si (i)/a-Si (n)/ITO/Spiro-TTB/FA _{1-x} Cs _x Pb(I,Br _{0.2}) ₃ /LiF/C ₆₀ /SnO ₂ /IZO/PDMS	1.788	19.5	73.1	25.52 (25.24)	46
2018	Al/ITO/ n -type layer/a-Si:H (i)/ n -type Si/a-Si:H (i)/ p -type layer/TRL/ITO/SnO ₂ /Perovskite/Spiro-OMeTAD/MoO ₃ /ITO	1.71	15.87	74	20.1 (-)	67
2018	Ag/ZnO:Al/a-Si:H (p)/a-Si:H (i)/ n -type Si/a-Si:H (i)/nc-SiO _x :H/ITO/PTAA/Cs _{0.05} (FA _{0.83} MA _{0.17}) _{0.95} Pb(I _{0.83} Br _{0.17}) ₃ /C ₆₀ /SnO ₂ /IZO/ML foil	1.76 1.76*	18.5 19.4*	78.5 77*	25.2 26.5(26.5)*	69

2018	Al/ITO/nc-SiO _x :H (n)/a-Si:H (i)/n-type Si/a-Si:H (i)/nc-SiO _x :H (p)/TRL/ITO/SnO ₂ /Cs _{0.05} (FA _{0.83} MA _{0.17}) _{0.95} Pb(I _{0.7} Br _{0.3}) ₃ /Spiro-OMeTAD/MoO ₃ /ITO/AR	1.71	15.46	73	19.3 (-)	71
2018	(Ag/Al)/Cr/Pd/Ag/n ⁺ Si/n-type Si/p ⁺ Si/c-TiO ₂ /mp-TiO ₂ /Cs _{0.05} Rb _{0.05} FA _{0.765} MA _{0.135} PbI _{2.55} Br _{0.45} /PTAA or Spiro-OMeTAD/MoO _x /IZO/AR Foil	1.763	17.8	78.1	24.5 (24.1)	43
	(Ag/Al)/Cr/Pd/Ag/n ⁺ Si/n-type Si/SiO _x /a-Si (p)/c-TiO ₂ /mp-TiO ₂ /Cs _{0.05} Rb _{0.05} FA _{0.765} MA _{0.135} PbI _{2.55} Br _{0.45} /PTAA or Spiro-OMeTAD/MoO _x /IZO/AR Foil	1.703	17.2	79.2	23.2 (22.8)	
2019	Ti/Pd/Ag/ n ⁺⁺ Si/ n-type Si/p ⁺⁺ Si (Emitter)/SnO ₂ /MAPBI ₃ /Spiro-OMeTAD/MoO ₃ /ITO/Ag busbar/PDMS AR foil with (Ba,Sr) ₂ SiO ₄ :Eu ²⁺	1.732	16.5	81	23.1 (23)	53
2019	Ag/Al-BSF/p-type Si/n ⁺ Si (Emitter)/ITO/PTAA/(FAPbI ₃) _{0.85} (MAPbBr ₃) _{0.15} /PC ₆₁ BM/ZnO NP/IZO/LiF	1.645	16.12	79.92	21.19 (21.1)	55
2019	Ag/ITO/nc-SiC _x :F (p)/SiO _x /p-type Si /SiO _x / nc-SiC _x (n)/nc-Si (p ⁺)/Spiro-TTB/ FA _{1-x} Cs _x Pb(I,Br _{0.2}) ₃ /LiF/C ₆₀ /SnO ₂ /IZO/PDMS	1.741	19.5	74.7	25.41 (25.1)	54
2019	Ag/AZO/a-Si (p)/a-Si (i)/n-type Si/a-Si (i)/nc-SiO _x (n)/ITO/PTAA/Cs _{0.05} (FA _{0.83} MA _{0.17}) _{0.95} Pb(I _{0.83} Br _{0.17}) ₃ /C ₆₀ /SnO ₂ /IZO/LiF	1.78	17.81	78.64	24.95 (24.97)	66
2019	Ag/AZO/a-Si:H (p)/a-Si:H (i)/n-type Si/a-Si:H (i)/ITO/poly-TPD/Cs _{0.05} (FA _{0.83} MA _{0.17}) _{0.95} Pb(I _{0.83} Br _{0.17}) ₃ /ETL/Buffer layer/ITO/ARC	1.7919	19.02	74.6	25.43 (-)	68
2019	Ag/ITO/a-Si:H (p ⁺)/a-Si:H (i)/n-type Si/a-Si:H (n ⁺)/ITO/PTAA/Cs _{0.15} (FA _{0.83} MA _{0.17}) _{0.85} Pb(I _{0.8} Br _{0.2}) ₃ /ICBA/C ₆₀ /SnO ₂ /IZO/MgF ₂	1.8	17.8	79.4	25.4 (-)	72
2020	Ag/ITO/a-Si:H (p)/a-Si:H (i)/n-type Si/a-Si:H (n)/ITO/NiO _x /poly-TPD/PFN/ FA _{0.75} Cs _{0.25} Pb(I _{0.85} Br _{0.15}) ₃ +MAPbCl ₃ /LiF/C ₆₀ /SnO ₂ /ITO/PDMS	1.886	19.12	75.3	27.13 (27.04)	13
2020	Ag/ITO/a-Si:H (p)/a-Si:H (i)/n-type Si/a-Si:H (n)/IO _x /NiO _x /poly-TPD/ Cs _{0.05} FA _{0.8} MA _{0.15} PbI _{2.25} Br _{0.75} /LiF/C ₆₀ /SnO ₂ /IZO/MgF ₂	1.7805	19.07	75.36	25.59 (25.7)	47
2020	Ag/ITO/a-Si:H (p)/a-Si:H (i)/n-type Si/a-Si:H (n)/ITO/PTAA/Cs _{0.15} FA _{0.65} MA _{0.20} Pb(I _{0.8} Br _{0.2}) ₃ + PEAI _{0.25} SCN _{0.75} /C ₆₀ /PEIE/ITO	1.765	19.2	79.2	(26.7)	74

b) Perovskite/CIGS tandem photovoltaics

Among the emerging thin film photovoltaic technologies, I-III-VI type compound semiconductors consisting of copper, indium, gallium, sulphur and selenium are of significant interest. Consisting of a chalcopyrite crystalline structure, this technology displays a number of key advantages including high energy yield, low temperature coefficient of power loss, low sensitivity to shadowing (i.e. good performance under low illumination intensities as well as short energy payback times⁷⁵. Presently, CIGS PVs have achieved a certified Power Conversion Efficiency (PCE) of $23.35 \pm 0.5\%$ over areas of 1.043 cm^2 for lab scale devices while a certified PCE of $19.2 \pm 0.5\%$ over an aperture area of 841 cm^2 .⁷⁶

One of the important optoelectronic properties of CIGS is the tunability of its E_G ⁷⁷, with E_G in the range of 1.1 – 1.2 eV being the most widely developed. As a result, this allows the possibility of developing tandem solar cells when combined with absorbers with E_G in the range of 1.7 – 1.8 eV as allowed by perovskites.¹⁴ Despite this, there has been very little activity in developing 2T perovskite/CIGS tandem architectures as evident from the following discussion (related device performances given in [Table 2](#)).

The first example of a 2T perovskite/CIGS tandem device was reported by Todorov et al.⁷⁸ The authors evaluated the impact of both MAPbI₃ and MAPbBr₃ as the perovskite on the overall tandem performance. As the perovskite was observed to degrade when deposited on ZnO and annealed at 60 °C, the usage of an i-ZnO layer on the CIGS sub-cell was avoided. Furthermore, the perovskite sub-cell processing temperature was kept below 120° C to avoid the degradation of the CIGS sub-cell due to the interdiffusion that takes place at the cadmium sulfide (CdS)/CIGS interface. While the CIGS sub-cell on its own demonstrated a PCE of 11.6%, the authors noted a drop in the PCE to 4.6% with a J_{sc} of 16 mAcm⁻² when shadowed using an MAPbI₃ sub-cell. On the other hand, a higher PCE of 7.7% with a J_{sc} of 25 mAcm⁻² for the CIGS sub-cell was observed when shadowed with MAPbBr₃. Based on the above, the authors developed a perovskite with an E_G of 1.72 eV for the 2T tandem architecture. The perovskite was fabricated based on a vapour based halide exchange process where the existing halide was replaced by MABr vapour. Test devices formed using a 10-15 nm thick Al layer as the transparent conducting electrode (with 50% transmission) resulted in a PCE of ~8%. The authors pointed out a number of issues in this structure including the high resistance of the perovskite sub-cell, the high ideality factor of the overall tandem cell and the low optical transmission of the Al. Replacing the Al with a thin layer of Ca enabled a higher optical transmission of 70-80% which led to a PCE of 10.98%.

The next example of a 2T perovskite/silicon tandem devices was reported in 2018, possibly due to the difficulty in the fabrication of the perovskite cell on the highly textured CIGS which typically demonstrates a high σ_{RMS} of ~ 50 – 200 μ m.⁷⁹ In their work reported in 2018, Han et al.,⁸⁰ utilised a boron doped ZnO (BZO) layer on top of the CIGS cell which minimised the σ_{RMS} to ~60nm. However, this still possessed features with a height of ~250 nm. In order to address this, the authors deposited a thick layer of ITO which was then polished using a chemical-mechanical polishing (CMP) method ([Fig. 4\(a\)](#)) which reduced the height of the maximum vertical features observed to ~40nm. However, the thickness of the ITO was such that the CMP processing did not polish the BZO layer. As BZO has a work function of ~4 eV

in comparison to the PTAA hole transport layer (work function of -5.1 eV) used in this work, the use of an ITO layer reduced the barrier potential for holes, thereby enabling a more effective recombination junction to be formed. Following the CMP process, the CIGS cell was reported to show a slight decrease in J_{sc} to 34.34 mAcm⁻² from an initial value of 37.10 mAcm⁻² for the unpolished cell. This was attributed to the parasitic absorption due to the ITO over the wavelength region of 400 – 500 nm range (the parasitic absorption of ITO does not affect the absorption over longer wavelengths). The FF was also reported to decrease from 74.7% (unpolished) to 72.4% (polished), which was attributed to the higher sheet resistance (R_{sheet}) of the polished ITO. As a result, the CMP polishing process resulted in a decrease of the PCE to 16.76% from an initial value of 18.73% for the unpolished cell. The authors also noted a J_{sc} loss of 1.386 mAcm⁻² over the wavelength range of 750 – 1250 nm for the CIGS cell. For the perovskite sub-cell, the authors employed a Cs_{0.09}FA_{0.77}MA_{0.14}PbI_{2.58}Br_{0.42} (with E_G of 1.59 eV) as the absorber. In order to mitigate the detrimental influence of the prevailing surface roughness of the polished ITO, the authors optimized the thickness of the PTAA layer in combination with dopants. Following the above, the authors reported the fabrication of a 2T tandem cell where a certified PCE of 22.43% was achieved over a cell area of 0.042 cm² (Fig. 4(b)). The CIGS cell on this structure showed photocurrent losses over the wavelength range of 800 – 1100 nm (Fig. 4(c)) due to reflection losses at the ITO/air interface at the top cell, which was reduced using a MgF₂ antireflection, leading to a PCE of 20.8%. The stability of unencapsulated cells was observed by ageing the devices under ambient conditions for 500 h under 1-sun continuous illumination while maintaining the cell at 30 °C. The performance was observed to drop to a value of > 88% from an initial PCE of 22%. However, this loss was observed to be recoverable following storage of the cell in the dark for 12 hours. The high stability of the unencapsulated device under ambient conditions was attributed to use of ZnO and ITO which prevent moisture ingress⁸¹.

Despite the success in the above architecture developed by Han et al.,⁸⁰ one of the shortcomings was the requirement of a thick ITO layer which can result in parasitic absorption losses. To alleviate this shortcoming Jošt et al.⁷⁹ developed a bilayer HTL (Fig. 4(d)) for the perovskite based on a conformal NiO_x coating deposited using ALD (Fig. 4(e)), and PTAA. While NiO_x deposited using ALD requires annealing at 300 °C, this was avoided on the architecture reported as annealing at such high temperatures invariably results in interdiffusion at the CIGS/CdS interface. 2T tandem devices were based on the Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})₃ composition reported by Saliba et al.⁷ Tandem devices based on the bilayer

concept for the perovskite sub-cell showed a PCE of 21.6% with no hysteresis while devices that employed devices that used only PTAA or NiO_x showed lower PCEs of 3.1% and 18.2% respectively (Fig. 4(f)). External Quantum Efficiency (EQE) measurements carried out indicated a current mismatch of $\sim 2 \text{ mAcm}^{-2}$ indicating room for further improvement. Additionally, a further 2.62 mAcm^{-2} J_{sc} loss was identified due to reflection losses. Low parasitic absorption was observed between 400 – 1000 nm enabled by the highly transparent *n*-type contact. Parasitic absorption in the UV region dominated by absorption of C_{60} and IZO as well as absorption loss in CIGS near its band edge were identified as additional source of losses. In order to understand the losses in more detail, the authors fabricated single junction cells of CIGS consisting of a Ni/Al/Ni grid as the front contact which demonstrated a PCE of 16.3%. The authors noted alkali postdeposition treatment and light trapping schemes for improving the V_{oc} and J_{sc} respectively. Furthermore, based on estimation of the he quasi Fermi level splitting (QFLS) through hyperspectral PL imaging the authors noted that a V_{oc} of 1.70 V should be possible on elimination of loss mechanisms.

More recently, Al-alshouri et al.²⁴ reported the development of a new class of hole transport layers based on self-assembled monolayers (SAMs) for perovskites which enabled a stable, high performance for CIGS-LHP 2T tandem cells. The SAMs reported; V1036 (2-{3,6-bis[bis(4-methoxyphenyl)amino]-9H-carbazol-9-yl}ethyl)phosphonic acid (V1036), MeO-2PACz [2-(3,6-dimethoxy-9H-carbazol-9-yl)ethyl]phosphonic acid (MeO-2PACz) and [2-(9H-carbazol-9-yl)ethyl]phosphonic acid (2PACz) were based on carbazole derivates that enable transportation of holes while the localization of electrons. Additionally, the phosphonic acid groups were incorporated to these SAM materials which enables a self-limiting adhesion process to ITO. The authors evaluated the above hole transport layers in perovskite/CIGS tandem PVs, using AZO/SAM (formed by dip coating) recombination junction. The resulting tandem devices showed an impressive certified PCE of 23.26% over an area of 1.03 cm^2 which exceeded the PCE of 21.6% for perovskite/CIGS tandems incorporating the NiO_x /PTAA bilayer⁷⁹. Notably, the bottom cell alone demonstrated a PCE of 15 – 16% while the V_{oc} was improved compared to the previous work from 1.59 V⁷⁹ to 1.68 V. However, the FF was reduced to 72% compared to 76% obtained for the NiO_2 /PTAA double layer.

The development of perovskite/CIGS tandems have also been expanded to the fabrication of flexible 2T tandem architectures where the MAPbI_3 perovskite sub-cell was processed on a CIGS cell that had been fabricated on a polyimide foil.⁸² A thin PTAA layer that was doped with 1 wt.% F4TCNQ was used as the hole transport layer for the perovskite sub-cell. Unlike

the work reported by Jošt et al.,⁷⁹ the authors reported the formation of a conformal coating of PTAA on the somewhat rough, CIGS cell. A Ni-Al metal grid was also utilized on the AZO top transparent contact to enable better charge collection, while a MgF₂ anti-reflection coating was incorporated to reduce reflectance losses. A steady state PCE of 13.2% was reported with very little V_{oc} loss indicating the formation of a good recombination junction. However, the overall performance was limited by the sub-optimal photocurrent generation in the MAPbI₃ layer due to its thickness of < 300 nm which does not enable all the incident photons above its E_G to be absorbed. Additionally, a lower charge collection efficiency was observed for the LHP in the tandem configuration compared to its single junction variant indicating a collection loss. One possible source for this loss was attributed to the small grain size which is lower than the film thickness. Interestingly, despite the potential for such perovskite/CIGS flexible devices with improved performances, especially in light of recent developments in multi-cation perovskite absorbers, there has been very little work published so far in this regard.

Beyond the application of terrestrial applications, Lang et al.⁸³ evaluated perovskite/CIGS tandem PVs for space-based energy harvesting (Fig. 4(g)). The resulting devices retained 85% of its initial performance, even after irradiation under 68 MeV protons with a cumulative dose of $\sim 10^{12}$ protons/cm² (Fig. 4(h) and (i)). The degradation in performance was attributed to increase in carrier recombination in the CIGS sub-cell and the NiO_x layer used in the bilayer hole transport system used for the perovskite sub-cell. In comparison, the PCE of perovskite/silicon tandems were observed to decrease to 1% of its initial value under similar irradiation conditions. The high radiation stability of the perovskite is in agreement with their application as an emerging system for direct conversion radiation detectors^{84,85} and points towards a new field of application for these tandem devices.

Fig. 4 (a) The chemical mechanical polishing (CMP) method used by Han et al.⁸⁰ to reduce the surface roughness of the CIGS sub-cell. (b) indicates the J - V characteristics of the perovskite/CIGS tandem formed where the CIGS sub-cell surface was smoothened using the CMP process and (c) the EQE spectra for each sub-cell for the above tandem device. The MPPT for the optimized device is shown on the inset for panel (b). From Ref. 80. Reprinted with permission from AAAS. (d) High-angle annular dark-field scanning transmission electron micrograph cross-section of the perovskite/CIGS tandem device reported by Jošt et al.⁷⁹ The related EDX image for Ni indicating the conformal coating of NiO_x on the CIGS sub-cell is given in (e) and (f) shows the tandem device performance for devices that utilized only PTAA, only NiO_x and NiO_x/PTAA bilayer. The MPPT for the optimized device is shown on the inset. Reprinted with permission from Ref. 79. Copyright (2019) American Chemical Society. (g) Schematic of the perovskite/CIGS tandem architecture evaluated for radiation stability by Lang et al.⁸³ and the energy deposition profile for 68 MeV protons for the same architecture. (h) J - V characteristics for the above tandem device under AM1.5G and AM0 spectra, before and after proton irradiation. The MPPT tracking under both spectra before and after irradiation is shown in the inset. (i) The EQE spectra of the individual sub-cells before and after proton irradiation. The CIGS sub-cell is observed to have the highest lost in photocurrent. Reprinted from Ref. 83 under the Creative Commons CC-BY license.

Table 2. Summary of performance characteristics for perovskite/CIGS tandem photovoltaics. SPO indicates stabilised power output.

Year	Configuration	V_{oc} (V)	J_{sc} (mAcm^{-2})	FF	PCE (%) (SPO(%))	Ref
2015	glass/ Si_3N_4 /Mo/CIGS/CdS/ITO/PEDOT:PSS/MAPb(I,Br) ₃ /PC ₆₁ BM/Al	1.315	8.9	68.9	8 (-)	78
	glass/ Si_3N_4 /Mo/CIGS/CdS/ITO/PEDOT:PSS/MAPb(I,Br) ₃ /PC ₆₁ BM/Ca	1.45	12.7	56.6	10.9 (-)	
2018	glass/Mo/CIGS/CdS/i-ZnO/BZO/ITO/PTAA/PVSK/PC ₆₁ BM/ZnO NP/ITO/MgF ₂	1.774	17.3	73.1	22.43	80
2019	glass/Mo/CIGS/CdS/ZnO/NiO _x /PTAA/Cs _{0.05} (FA _{0.83} MA _{0.17}) _{0.95} Pb _{1.1} (I _{0.83} Br _{0.17}) ₃ /C ₆₀ /SnO ₂ /IZO/LiF	1.58	18	76	21.6 (21.6)	79
2019	glass/Mo/CIGS/CdS/ZnO/SAM/Cs _{0.05} (FA _{0.83} MA _{0.17}) _{0.95} Pb(I _{0.83} Br _{0.17}) ₃ /C ₆₀ /SnO ₂ /IZO/LiF	1.68	19.17	71.9	23.16 (23.26)	24
2020	glass/Mo/CIGS/CdS/ZnO/NiO _x /PTAA/Cs _{0.05} (FA _{0.83} MA _{0.17}) _{0.95} Pb(I _{0.83} Br _{0.17}) ₃ /C ₆₀ /SnO ₂ /IZO/LiF	1.52	16.7	70.8	18 (18)	86

c) All perovskite tandem photovoltaics

As mentioned previously, one of the key advantages of perovskite semiconductors is their bandgap tunability. While the development of wide E_G has attracted a significant interest, there is now a growing activity in terms of developing narrow E_G perovskites through the partial or complete replacement of Pb^{2+} with Sn^{2+} . The slow development of this technology has been mainly due to the undesirable oxidation of Sn^{2+} to Sn^{4+} , even when processed under glove box conditions. However, recent activities as discussed later-on have identified routes to mitigate this issue to some extent, enabling high performing single junction low band E_G perovskite devices as well as all-perovskite tandem architectures to be developed, hinting the possibility for an all printed perovskite PV technology. In the discussion below, we highlight the key developments that have taken place in this area including devices which incorporate Pb-only perovskite absorbers. Related device performances are summarized in [Table 3](#).

Due to the early development in E_G tunability in lead-only PSCs, 2T tandem architectures incorporating Pb-only perovskites were the first reported all-perovskite 2T tandem architecture. For this, Heo et al.⁸⁷ used a top cell made of MAPbBr₃ ($E_G = 2.25$ eV) and a bottom cell made of MAPbI₃ ($E_G = 1.55$ eV) where the tandem cell was fabricated by simply sandwiching the two substrates containing the top and bottom cells together by pressuring with a double clip and subsequent drying. Based on this simple methodology, they were able to fabricate a monolithic tandem with PCE of 10.8% and V_{oc} of 1.95 V. One of the biggest

challenges faced in the fabrication of a 2T tandem PV is the optimization of the charge recombination junction or the interconnecting layers (ICLs) between the top and bottom cells so as to a) avoid voltage losses, b) act as a barrier that prevents the dissolution of the bottom cell when depositing the top cell and c) minimise optical losses. In the above work by Heo et al.⁸⁷ the clipping of cell prevented the dissolution of one cell. However, in terms of manufacturability and performance optimisation, it would be preferable for such an approach to be avoided. The first bottom-up fabricated 2T all-perovskite tandem PV was demonstrated by Jiang et al.⁸⁸ where a solution processed charge recombination layer made of Spiro-OMeTAD/Poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS)/Polyethyleneimine (PEI)/(PC₆₁BM):PEI was used to serially bridge the top and bottom cells was used. By using these recombination layers and top and bottom cells made of MAPbI₃, they were able to achieve a PCE of 7% and V_{OC} of 1.89 V, which was almost equal to the sum of V_{OC} 's of the two sub cells.

Forgács et al.⁸⁹ later reported a 2T tandem architecture based on the double cation Cs_{0.15}FA_{0.85}Pb(I_{0.3}Br_{0.7})₃ as the wide bandgap absorber (with $E_G = 2$ eV) and MAPbI₃ as the low bandgap absorber ($E_G = 1.55$ eV). In their work, N₄,N₄,N₄'',N₄''-tetra([1,1'-biphenyl]-4-yl)-[1,1':4',1''-terphenyl]-4,4''-diamine (TaTm), doped with 2,2'-(perfluoronaphthalene-2,6-diylidene) dimalononitrile (F6-TCNNQ) and C₆₀ doped with N1,N4-bis(tri-p-tolylphosphoranylidene) benzene-1,4- diamine (PhIm) was used as the interconnecting layer (ICL). The resulting devices demonstrated a champion PCE of 18.1% with an impressive V_{OC} of 2.1 V, most likely due to improved optoelectronic characteristics in the dual cation 2 eV wide E_G cell used.

One of the major milestones in the field of all-perovskite 2T tandem architectures was reported by Eperon et al.⁹⁰ where they combined a wide bandgap FA_{0.83}Cs_{0.17}Pb(I_{0.5}Br_{0.5})₃ ($E_G = 1.8$ eV) with a narrow bandgap sub-cell consisting of the Pb-Sn mixed perovskite system FA_{0.75}Cs_{0.25}Pb_{0.5}Sn_{0.5}I₃ ($E_G = 1.22$ eV) to form tandem architectures. The resulting monolithic devices fabricated also employed a recombination junction consisting of SnO₂ and ZTO together with and sputtered indium tin oxide (ITO) which acted as a barrier, that protects the underlying perovskite from any solvent damage that occur during subsequent processing. The resulting 2T tandem device demonstrated an impressive PCE of 17% enabled by a high $V_{OC} > 1.65$ V. The authors noted the impressive stability of the Pb-Sn mixed composition reported here, where the device stability was identified to be on par with that of Pb-only devices with no reduction in performance when held at maximum power-point (MPP) in an inert (nitrogen)

environment for more than 18 hours. Following this, Leijten et al.⁹¹ reported a 2T tandem architecture where a wide E_G $\text{Cs}_{0.4}\text{FA}_{0.6}\text{Pb}(\text{I}_{0.7}\text{Br}_{0.3})_3$ was combined with the $\text{FA}_{0.75}\text{Cs}_{0.25}\text{Pb}_{0.5}\text{Sn}_{0.5}\text{I}_3$ low E_G absorber enabling a PCE of 19.1% to be achieved (Fig. 5(a) and (b)). The improvement in PCE was achieved through better current matching between the two sub-cells and the post deposition treatment of the narrow bandgap absorber with methylammonium chloride (MACl) of the low bandgap absorber, which improved the perovskite crystallization and increased the grain size, ultimately leading to an increase in the V_{OC} and fill FF .

Rajagopal et al.⁹² developed a tandem architecture based on $\text{MAPb}_{0.5}\text{Sn}_{0.5}\text{I}_3$ as the low bandgap absorber (with $E_G = 1.2$ eV) and $\text{MA}_{0.9}\text{Cs}_{0.1}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ as the wide bandgap absorber (with $E_G = 1.8$ eV). Among the key developments of this work involved a) the identification of indene-C60 bis-adduct as a more matching electron transport layer (ETL) for the Pb-Sn mixed absorber and b) the development of an ICL based on Bis-C₆₀/ITO/PEDOT:PSS which enabled a high V_{OC} of 1.98 V which is 80% of the value predicted by the Shockley-Queisser limit resulting in a PCE of 18.5%.

The next notable improvement in 2T all perovskite tandem solar cells was reported by Zhao et al.⁹³ In their work, they utilised a composition of $(\text{FASnI}_3)_{0.6}(\text{MAPI}_{3-3x}\text{Cl}_{3x})_{0.4}$ for the low bandgap ($E_G = 1.25$ eV). The incorporation of chloride ions, similar to Leijten et al.⁹¹ resulted in an increase in the grain size which is compatible with the film thickness of ~750 nm, as well as a reduction in the trap density. This low bandgap cell when combined with a wider bandgap absorber based on the $\text{FA}_{0.8}\text{Cs}_{0.2}\text{Pb}(\text{I}_{0.7}\text{Br}_{0.3})_3$ composition ($E_{BG} = 1.75$ eV) through a Ag(1 nm)/MoO₃(3 nm)/ITO(120 nm) ICL led to the first demonstration of a PCE exceeding 20% (20.6%) for all-perovskite 2T tandem architectures (Fig. 5(c)). These cells also demonstrated an impressive stability with 80% of its initial PCE being maintained after 80 hours of continuous illumination under AM1.5G conditions in air without encapsulation while the cells retained 94% of its initial PCE after 45 days of storage in ambient air (Fig. 5(d)).

Subsequent to this, there have been several rapid developments within a short span that has enabled further improvements in 2T tandem architectures consisting of a wide bandgap Pb only cell in combination with a narrow bandgap Pb-Sn mixed sub-cell. Among the developments made include processing optimisation for thicker Pb-Sn mixed perovskite sub-cells and reduction of background carrier density. For example, Tong et al.⁹⁴ reported the incorporation of guanidinium thiocyanate into the $(\text{FASnI}_3)_{0.6}(\text{MAPbI}_3)_{0.4}$ which enabled a significant

improvement in the carrier lifetimes to $> 1 \mu\text{s}$ and also the reduction of the background carrier concentration by and order of magnitude, enabling the fabrication of thick absorber layers for increased light harvesting, especially in the near-infrared portion. This low bandgap cell when coupled with an $E_G = 1.63 \text{ eV}$ wideband gap sub-cell with a composition of $\text{Cs}_{0.05}\text{FA}_{0.80}\text{MA}_{0.15}\text{PbI}_{2.55}\text{Br}_{0.45}$ enabled a champion PCE of 18%. By changing the wide bandgap absorber to a perovskite with $E_G = 1.75 \text{ eV}$, a significantly improved PCE of 23.4% was obtained while more than 88% of the initial PCE was maintained under continuous AM1.5G illumination for 100 hours. These devices demonstrated an impressive FF exceeding 80% as well as a V_{OC} of 1.942 V.

While the above activities enabled PCE improvements in all-perovskite tandem devices, the oxidation of Sn^{2+} (the preferred oxidation state for PSCs) to Sn^{4+} remained a challenge with approaches such the inclusion of SnF_2 , use of appropriate anti-solvent washing and annealing temperatures¹¹ being utilised to mitigate this issue. Recently, Lin et al.¹² outlined a comproportionation process where Sn powder is added to the precursor mix enabling the reduction of Sn^{4+} to Sn^{2+} thereby minimising the detrimental impact of Sn^{2+} oxidation. Based on this method, a single junction PSC based on the $\text{FA}_{0.7}\text{MA}_{0.3}\text{Pb}_{0.5}\text{Sn}_{0.5}\text{I}_3$ absorber achieved a PCE of 21% PCE while combining this with a wide bandgap $\text{Cs}_{0.2}\text{FA}_{0.8}\text{PbI}_{1.8}\text{Br}_{1.2}$ absorber to form monolithic 2T tandem solar cell (Fig. 5(e)) resulted in a certified PCE of 24.8% for an aperture area of 0.073 cm^2 (Fig. 5(f)) and 22.3% for an aperture area of 1.03 cm^2 . These are the highest reported for a 2T all perovskite tandem solar cell as of present. These devices also demonstrated an impressive stability where 90% of its initial performance was maintained after 463 hours of operation (Fig. 5 (g)).

Perhaps one of the first demonstrations on fabrication of all perovskite tandem solar cells fabricated on flexible substrates was reported by Palmstrom et al.⁹⁵ In their work ALD was used to grow the recombination layers of the monolithic tandem in order to reduce shunting and damage caused to the underlying layers due to solvents used in subsequent processing of the tandem cell. Hence, an ALD grown aluminium doped zinc Oxide (AZO) layer was grown on top of C_{60} using an ultra-thin (1 nm) nucleation layer in the form of poly(ethylenimine) ethoxylated (PEIE). However, they also discovered that a thin layer of transparent conductive oxide (TCO) is required to prevent FF losses due to damage caused to the AZO layer by acidic PEDOT:PSS. 2T tandem architectures were fabricated on a flexible IZO coated polyethylene naphthalate (PEN) substrate in the configuration of PEN/Sputtered IZO/Poly-TPD/PFN/ $\text{FA}_{0.6}\text{Cs}_{0.3}\text{DMA}_{0.1}\text{PbI}_{2.4}\text{Br}_{0.6}/\text{LiF}/\text{C}_{60}/\text{PEIE}/\text{AZO}/\text{IZO}/\text{PEDOTT:PSS}/\text{FA}_{0.75}\text{Cs}_{0.25}\text{Sn}_{0.5}\text{Pb}_{0.5}\text{I}_3/$

C₆₀/ BCP/ Au which resulted in a PCE of 21.3% (with 23.1% on a glass substrate) with a V_{OC} of 1.82 V and a FF of 75%. The devices also maintained more than 95% of its initial performance after 100 bend cycles (bend radius of 1.5 cm). Furthermore, no degradation was observed when continuously illuminated under AM1.5G for 13 hours as well as when stored in the dark at 85° C for 50 h.

In terms of other developments with regards to appropriate ICL layers, Chang et al.⁸⁶ developed an ICL based on a cross-linkable p-doped PTAA layer and PCBM. As the cross-linking agent, 1,2-bis[4-(azidomethyl)phenyl]- 1,2-diphenylethene (TPE-MN3) was employed while molybdenum tris-[1-(trifluoroethanoyl)-2-(trifluoro- methyl)ethane-1,2-dithiolene] (Mo(tfdCOCF₃)₃) was incorporated as the p-type dopant. The incorporation of TPE-MN3 enabled cross linking of PTAA under UV irradiation, resulting in a dense blocking layer that has better solvent-resistance, thereby protecting the underlying perovskite absorber when processing the top perovskite absorber. The devices based on a regular architecture (as opposed to the inverted architecture widely used for all perovskite 2T tandem structures) which combines MAPbI₃ as the wide bandgap absorber and MAPb_{0.75}Sn_{0.25}I₃ as the low bandgap absorber resulted in a champion PCE of 18.69%, with a stabilized PCE of 18.92%. Most notably, the V_{OC} of the tandem architecture (1.79 V) was exceptionally close to the sum of the V_{OC} s of individual sub-cells (1.80 V) indicating the effectiveness of the ICL developed.

Going beyond the widely explored 2T-2J concept, McMeekin et al.⁹⁶ demonstrated a 2T-3J (triple junction) architecture based on 3 perovskite light absorption layers, namely; FA_{0.83}CS_{0.17}Pb(I_{0.3}Br_{0.7})₃ (E_G = 1.94 eV) in the top cell, MAPbI₃ (E_G = 1.57 eV) in the middle cell and MAPb_{0.75}Sn_{0.25}I₃ (E_G = 1.34 eV) in the bottom. While optical modelling showed that the cell had a potential of achieving a PCE of around 26.7% and a corresponding V_{OC} of 3.16 V, the fabricated device only showed a PCE of 6.7% and a V_{OC} of 2.7 V. Despite being significantly lower than the anticipated values, it can be envisioned that significant improvements in performance as being possible following the optimisation of interconnecting layers to reduce parasitic absorptions etc. This work so far remains the only reported work for 2T-3J all-perovskite tandem devices.

Fig. 5 (a) Schematic of the cross-sectional scanning electron micrograph of the device concept used by Leijten et al.⁹¹ in their all perovskite 2T tandem architecture. The *J*-*V* characteristic of this tandem devices is given in (b). Reproduced from Ref. 91 with permission from The Royal Society of Chemistry. (c) The *J*-*V* characteristics of the wide bandgap, narrow bandgap single junction PSCs and the resulting tandem device incorporating MACl and (d) the maximum power point tracking of the same as reported by Zhao et al.⁹³ Reproduced from Ref. 93 with permission from Springer Nature. (e) The schematic and cross sectional scanning electron micrograph of all perovskite 2T tandem device reported by Lin et al.¹² where the use of Sn powder to reduce the detrimental effect of oxidation of Sn²⁺ resulted in a PCE of 24.8% as indicated by (f) the *J*-*V* characteristics. (g) The maximum power tracking carried out for 463 h for this device. Reproduced from Ref. 12 with permission from Springer Nature.

Table 3. Summary of performance characteristics for all perovskite tandem photovoltaics. SPO indicates stabilised power output.

Year	Configuration	V_{oc} (V)	J_{sc} (mAcm ⁻²)	FF	PCE (%) (SPO(%))	Ref
2015	Glass/FTO/c-TiO ₂ /MAPbBr ₃ /P3HT/PCBM/MAPbI ₃ /PEDOT:PSS/ITO	1.95	8.4	66	10.8 (-)	87
	Glass/FTO/c-TiO ₂ /MAPbBr ₃ /PTAA/PCBM/MAPbI ₃ /PEDOT:PSS/ITO	2.25	8.3	56	10.4 (-)	
2016	Glass/FTO/c-TiO ₂ /mp-TiO ₂ /MAPbI ₃ /Spiro-OMeTAD/PEDOT:PSS/PEI/PCBM:PEI/ MAPbI ₃ /Spiro-OMeTAD/hc-PEDOT:PSS	1.89	6.61	56	7 (-)	88
2016	Glass/ITO/NiO/FA _{0.83} CS _{0.17} Pb(I _{0.5} Br _{0.5}) ₃ /ZTO/SnO ₂ /PCBM/ITO/PEDOT:PSS/FA _{0.75} CS _{0.25} Sn _{0.5} Pb _{0.5} I ₃ /(C ₆₀ /BCP)/Ag	1.66	14.5	70	16.9 (14.8)	90
2016	ITO/TiO ₂ /IPH/CS _{0.15} FA _{0.85} Pb(I _{0.3} Br _{0.7}) ₃ /TaTm/TaTm:F6-TCNNQ/C ₆₀ :PhIm/C ₆₀ /MAPbI ₃ /TaTmTaTm:F6-TCNNQ/Ag	2.29	9.83	80.3	18.1 (14.5)	89
2017	Glass/ITO/NiO/MA _{0.9} CS _{0.1} Pb(I _{0.6} Br _{0.4}) ₃ /C ₆₀ /Bis-C ₆₀ /Sputtered ITO/PEDOT:PSS/ MAPb _{0.5} Sn _{0.5} I ₃ /IC ₆₀ BA/Bis-C ₆₀ /Ag	1.98	12.7	73	18.4 (18.5)	92
2018	Glass/ITO/PTAA/FA _{0.6} CS _{0.4} Pb(Br _{0.3} I _{0.7}) ₃ /C ₆₀ /SnO ₂ /sputtered ITO/PEDOT:PSS/FA _{0.75} CS _{0.25} Sn _{0.5} Pb _{0.5} I ₃ /C ₆₀ /BCP/Ag	1.81	14.8	70	19.1 (19.1)	91
2018	Glass/ITO/TiO ₂ /C ₆₀ /MAPbI ₃ /TaTm/TaTm:F6-TCNNQ/C ₆₀ :PhIm/C ₆₀ /MAPbI ₃ /TaTm/TaTm:F6-TCNNQ/Au	2.3	9.84	79.58	18.02 (-)	97
2018	Glass/ITO/NiO/FA _{0.83} CS _{0.17} Pb(Br _{0.5} I _{0.5}) ₃ /FSIP/C ₆₀ /BCP/Cu/Au/PEDOT:PSS/FA _{0.5} MA _{0.5} Pb _{0.5} Sn _{0.5} I ₃ /polystyrene/C ₆₀ /BCP/Ag	1.72	12.8	73	16.07 (16.1)	98
2018	Glass/ITO/PTAA/FA _{0.6} CS _{0.4} Pb(Br _{0.3} I _{0.7}) ₃ /C ₆₀ /BCP/Ag/MoOx/sputtered ITO/PEDOT:PSS/FA _{0.75} CS _{0.25} Sn _{0.5} Pb _{0.5} I ₃ /Cl/C ₆₀ /BCP/Ag	1.92	14	78.1	21 (20.7)	93
2019	Glass/FTO/SnO ₂ /PC ₆₁ BM/FA _{0.83} CS _{0.17} Pb(I _{0.3} Br _{0.7}) ₃ /Spiro-OMeTAD/PEDOT:PSS/ITO NPs/ PC ₆₁ BM /MAPbI ₃ /Spiro-OMeTAD/Ag	2.18	11.5	63	15.2 (15.2)	96
	Glass/FTO/SnO ₂ /PC ₆₁ BM/FA _{0.83} CS _{0.17} Pb(I _{0.3} Br _{0.7}) ₃ /Spiro-OMeTAD/PEDOT:PSS/ITO NPs/PC ₆₁ BM/MAPbI ₃ /Spiro-OMeTAD/PEDOT:PSS/ITO NPs/ PC ₆₁ BM /MAPb _{0.75} Sn _{0.25} I ₃ /Spiro-(TFSI) ₂ /Ag	2.7	8.3	43	6.7 (6.4)	
2019	Glass/ITO/PTAA/CS _{0.05} FA _{0.8} MA _{0.15} PbI _{2.55} Br ₄₅ /C ₆₀ /SnO ₂ /ZTO/Sputtered IZO/PEDOT:PSS/GuaSCN-modified (FASnI ₃) _{0.6} (MAPbI ₃) _{0.4} /C ₆₀ /BCP/Ag	1.94	15.01	80.31	23.4(23.1)	94
2019	Glass/ITO/Poly-TPD/PFN/FA _{0.6} CS _{0.3} DMA _{0.1} PbI _{2.4} Br _{0.6} /LiF/C ₆₀ /PEIE/AZO/IZO/PEDOT:PSS/FA _{0.75} CS _{0.25} Sn _{0.5} Pb _{0.5} I ₃ /C ₆₀ /BCP/Au	1.88	16	77	23.1 (23)	95
	PEN/Sputtered IZO/PolyTPD/PFN/FA _{0.6} CS _{0.3} DMA _{0.1} PbI _{2.4} Br _{0.6} /LiF/C ₆₀ /PEIE/AZO/IZO/PEDOT:PSS/FA _{0.75} CS _{0.25} Sn _{0.5} Pb _{0.5} I ₃ /C ₆₀ /BCP/Au	1.82	15.6	75	21.3 (21.3)	
2019	Glass/ITO/PTAA/CS _{0.2} FA _{0.8} PbI _{1.8} Br _{1.2} /C ₆₀ /ALD-SnO ₂ /Au/PEDOT:PSS/FA _{0.7} MA _{0.3} Pb _{0.5} Sn _{0.5} I ₃ /C ₆₀ /BCP/Cu	1.96	15.6	81	24.8 (24.5)	12
2019	Glass/ITO/TiO _x /PC ₆₁ BM/MAPbI ₃ /p-doped crosslinked PTAA/HMB-doped PC ₆₁ BM/MASn _{0.25} Pb _{0.75} I ₃ /p-doped crosslinked PTAA/Ag	1.79	13.36	78.18	18.69 (18.92)	99

d) Perovskite/organic tandem photovoltaics

Organic BHJ PVs is perhaps one of the earliest PV technologies to adopt printing technologies. Despite this, perovskite-organic bulk heterojunction (BHJ) tandem devices are a relatively less well explored concept compared to the more widely investigated perovskite incorporated tandem architectures which employ either Si, copper indium gallium selenide or even a perovskite as the low bandgap absorber. While initial tandem device concepts were based on combining two BHJ absorbers, the field was somewhat restricted in terms of the possible performance due to Voltage losses as high as 0.6 V^{100,101} and the lack of efficient infrared absorbers, recent developments in the field^{102,103} has resulted in the development of high performing single junction architectures with absorption up to ~ 1000 nm^{104,105} while the Voltage losses have now been significantly reduced^{101,106}. This has led to significant improvements in single junction device efficiencies which now exceed 16%.^{107,108} As a result, there is now growing interest towards the formation of tandem architectures by combining organic BHJs with perovskites as discussed below (A summary of reported device performances are given in [Table 4](#)).

In terms of perovskite/organic BHJ 2T tandem architecture, the first work in this regard was reported by Chen et al.¹⁰⁹ In their work, the authors used MAPbI₃ as the wide E_G absorber while a BHJ consisting of PBSeDTEG8 ($E_G = 1.28$ eV) as the donor and PC₆₁BM as the acceptor was used as the narrow E_G absorber. For the perovskite absorber, the authors reported the use of an additive assisted anti-solvent deposition method which enabled the formation of smooth pin-hole free absorber layers which resulted in a PCE of 9.1% for single junction PSCs. The use of the PBSeDTEG8 block copolymer-based donor was found to be beneficial in enabling better thermal stability for the BHJ absorber. Furthermore, this absorber did not necessitate the use of 1,8 diiodooctane (DIO), a commonly used additive in high performing organic BHJ devices, which can also result in poor shelf-life.¹¹⁰ The single junction organic BHJ sub-cell resulted in a PCE of 7%. Compared to the conventional 2T tandem architectures where the incident light first passes through the wide E_G absorber, this work employed an architecture where the light first passes through the narrow E_G BHJ absorber, a concept previously reported¹¹¹ for all organic BHJ tandem architectures. However, it is noted that such a device architecture is likely to result in undesirable absorption from the narrow E_G and result in sub-optimal performance. By employing an ICL consisting of poly[(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN)/PEDOT:PSS (high

conductivity, PH1000)/PEDOT:PSS (low conductivity, PVP AI 4083), the authors successfully demonstrated a 2T tandem device with a PCE of 10.2%.

Following this, Liu et al. reported¹¹² the development of a 2T perovskite-organic tandem device where the efforts were focused on the development of an ICL based on the stack of poly [(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN)/Al or Ag doped MoO₃ (step-layer)/MoO₃. The authors noted an improvement in the V_{OC} upon the incorporation of the step-layer. For example, when doped with Al, the V_{OC} was improved from 1.38 V to 1.45 V while this was further improved to 1.55 V upon using Ag as the dopant under optimized doping conditions. Furthermore, the use of dopants was also reported to result in the elimination of an *S-shaped J-V* characteristic for the tandem device which is indicative of a more balanced charge transport through the device. Following a 2T tandem device architecture incorporating MAPbI_{3-x}Cl_x as the wide bandgap absorber and poly{2,6'-4,8-di(5-ethylhexylthienyl)benzo[1,2-b;3,4-b]dithiophene-alt-5,5'-dibutyloctyl-3,6-bis(5-thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4-dione}(PBDTT-DPP): [6,6]-Phenyl C71 butyric acid methyl ester (PC₇₁BM) as the narrower bandgap absorber, a PCE of 8.62% was achieved based on further optimization of the individual layers. In the above, the removal of *S-shaped J-V* characteristics following the inclusion of Ag as a dopant indicates the need for careful optimization of individual layers as well as the recombination junction to achieved balanced currents from individual sub-cell.

A significantly improved PCE of 16% for perovskite-BHJ 2T tandems was subsequently reported by Liu, et al.¹¹³ In this work, the authors used MAPbI₃ absorber processed using the acetate route¹¹⁴ on a heated substrate temperature and a Poly([2,6'-4,8-di(5-ethylhexylthienyl)benzo[1,2-b;3,3-b]dithiophene]{3-fluoro-2[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl}) (referred to as PCE10 or PTB7-Th or PBDTTT-EFT or PBDTT-FTTE): PC₇₁BM as the BHJ based absorber (Fig. 6(a)-(c)). We note several key developments that enabled the high PCE for this 2T tandem architecture. Firstly, an ICL based on tris(sulfobetaine)-substituted fulleropyrrolidine (C₆₀-SB)/ultra-thin Ag/MoO₃ was used. The C₆₀-SB layer processed using 2,2,2-trifluoroethanol as the solvent does not dissolve the underlying layers in the perovskite sub-cell and in combination with the ultrathin Ag and MoO₃ layers, acts as a barrier against solvent induced dissolution of the perovskite sub-cell when processing the BHJ sub-cell. Additionally, based on Kelvin Probe Force Microscopy (KPFM) analysis, a favourable potential gradient was identified enabling electron extraction from the perovskite sub-cell into the C₆₀-SB layer and the extraction of holes from the BHJ sub-cell into the MoO₃ layer. While the PCE10:PC₇₁BM sub-cell utilized DIO, the detrimental

impact of this additive¹¹⁰ was eliminated through vacuum based removal of DIO in the BHJ layer. Finally, the thickness of the perovskite absorber was tuned in the range of 70 – 160 nm (significantly lower than that used for single junctions' PSCs) while maintaining a constant thickness of 100 nm for the PCE10:PC₇₁BM layer enabling an improvement in V_{OC} and J_{SC} to be achieved.

Zeng et al.¹¹⁵ utilized the concept of an all inorganic perovskite absorber coupled with a BHJ to form a 2T tandem device. In their work, the CsPbI₂Br perovskite sub-cell was coupled with the high performing ternary BHJ system of PTB7-Th: 2,2'-[[4,4,11,11-tetrakis(4-hexylphenyl)-4,11-dihydrothieno[2',3':4,5]thieno[2,3-d]thieno[2''',3''':4'',5'']thieno[2''',3''':4'',5'']pyrano[2'',3'':4',5']thieno[2',3':4,5]thieno[3,2-b]pyran-2,9-diyl]bis[methyldiyne(5,6-difluoro) (or COi8DFIC):PC₇₁BM, a BHJ system used to demonstrate the highest all-organic 2T tandem architecture reported so far³⁷. Using an ICL of MoO₃/Au/ZnO, a PCE of 15.04% was reported with the overall performance being limited due to low current in the perovskite sub-cell. However, considering recent developments for the all-inorganic perovskite single junction devices^{6,116,117}, further improvements in the above tandem architectures can be anticipated.

Compared to the above device architectures where an ICL layer is incorporated in forming a 2T tandem architecture, there have also been reports on an “integrated” concept where the ICL layer is eliminated (Fig 6(d)). Not only does this enable complementary absorption to be incorporated during the design, this also eliminates the need for complicated processing for the deposition of an ICL, thereby simplifying the overall stack. Although this device architecture is perhaps not a tandem configuration as per the conventional usage of the term, we nevertheless discuss important developments in this area as it presents an opportunity to enhance the spectral response and perhaps improve tandem architectures based on Pb-only compositions.

The first reported work in this regard was by Liu et al.¹¹⁸ where a small molecule organic BHJ based on DOR3T-TBDT: PC₇₁BM was spin coated on an MAPbI_{3-x}Cl_x perovskite absorber. Compared to semiconducting polymers, small molecule systems have been identified as an alternate that minimises performance variations due to factors such as the broad distribution in molecular weight as prevalent in semiconducting polymers.^{119,120} The device developed Liu et al.¹¹⁸ resulted in an overall device PCE of 14.3% (Fig 6(e)). As the absorption of the BHJ used overlaps with the perovskite absorber thereby making it difficult to identify the exact influence of the above architecture, the authors utilised a low bandgap BHJ architecture based on

PBDTT-SeDPP (the selenised form of PBDTT-DPP): PC₇₁BM as the BHJ which also demonstrated a PCE of 12% (Fig. 6(f)). In the above architecture, the authors attributed the observed performance as being due to the donor phase in the BHJ acting as a hole transport layer for perovskite while the perovskite acts as an electron accepting system for the charges generated in the BHJ. The charge generation within the BHJ was identified to be important in terms of the overall device performance as a lower PCE was observed when only the donor polymer was used.

Following this, Kim et al.¹²¹ reported a perovskite and organic ternary BHJ based integrated device with a PCE of 16.36% as compared to 14.7% efficient perovskite cells without a BHJ. The ternary BHJ was based on a blend consisting of the low bandgap polymer DT-PDPP2T-TT(TT) as the donor and poly{[N,N'-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-(2,2'-bithiophene)}(N2200) as well as PC₇₁BM as the acceptors. The authors also fabricated flexible integrated devices, taking advantage of the low temperature processing steps involved in this study, resulting in a champion PCE of 12%.

Cheng et al.¹²² utilised a small molecule BHJ architecture with a (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15} perovskite absorber. The authors evaluated several small molecule systems were designed based on the acceptor-donor-acceptor (A-D-A) concept where the phenoxazine flanked benzo[1,2b:4,5b']-dithiophene backbone was used for all molecules, but capped with different electron-withdrawing units; N-ethylrhodanine (for the molecule M1), N-(2-ethylhexyl)pyridinium (for the molecule M3), and (2-(3-cyano-5,5-dimethylfuran-2(5H)-ylidene)-malononitrile (for the molecule M4) which enabled the adjustment of the energy levels. While PSCs were tested through incorporation of the above small molecules as the HTL, an increase in the J_{SC} was observed when PC₇₁BM was incorporated to the organic material to form a BHJ. A champion PCE of 17.3% in reverse (average PCE of 16.2%) was achieved for the M3:PC₇₁BM BHJ incorporated device.

K. Gao et al.¹⁰⁵ reported the performance of integrated devices with MAPbI₃ as the perovskite and porphyrin donor based bulk heterojunction layer consisting of 5,15-bis(2,5-bis((2-ethylhexyl)thino)-3,6-dithienyl-2-yl)-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione-5'-yl-ethynyl)-10,20-bis(5-(2-ethylhexyl)thienyl)porphyrin zinc(II) (DPPZnP-TSEH): PC₆₁BM. As a result of the low bandgap of the organic donor, the authors were able to extend the absorption range of the perovskite and BHJ integrated stack up to the 900 nm which enabled a higher short circuit current density (J_{SC}) (of 23.32 mAcm⁻²) to be achieved in comparison to the above discussed work as well as the perovskite only reference device (J_{SC} of 21.37 mAcm⁻²), which

in turn enabled a PCE of 19.02%. Similar to the above Guo et al. reported¹²³ the use of an organic BHJ blend based on PBDTTT-E-T (PTB7): 2,2'-((2Z,2'Z)-((5,5'-(4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7-diyl)bis(4-((2-ethylhexyl)oxy)thiophene-5,2-diyl))bis(methanylylidene))bis(3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile which enabled an extended absorption up to 930 nm and an external quantum efficiency of 50% in the near-infrared range. This BHJ in combination with MAPbI₃ resulted in a high J_{SC} of 24.77 mAcm⁻², although the PCE was 14.57% (lower than the perovskite only device) due to a low FF . More recently, a ternary BHJ consisting of two donors: Y6 and S1 together with PCBM to enable absorption up to 980 nm (Fig 6(g) and (h))¹²⁴ was coupled with a triple cation perovskite CsFAMA resulting in a champion PCE of 20.61%, mainly due to the high J_{SC} of 28 mAcm⁻² as a result of the extension of the absorption (Fig 6(i)). Both of these reports indicate the possibility of the concept of spectral enhancement in Pb-only perovskite PVs by incorporation of newly emerging NIR absorbing organic semiconductors.

Fig. 6 (a) Schematic and (b) cross-section scanning electron micrograph of the perovskite-organic 2T tandem reported by Liu et al.¹¹³ resulting in a PCE of 16%. The insets show the C₆₀ based interfacial layer materials used. (c) The *J*-*V* characteristics for the best performing device for the above report. Reprinted with permission from Ref. 113. Copyright (2016) American Chemical Society. (d) Schematic indicating the charge generation and extraction process in a perovskite-organic integrated solar cell.¹¹⁸ The first reported devices in this work by Liu et al.¹¹⁸ where (e) DOR3T-TBDDT:PC₇₁BM and (f) PBDTT-SeDPP:PC₇₁BM BHJ layers were used. Reprinted with permission from Ref. 118. Copyright (2015) American Chemical Society. (g) The donor semiconductors used by Chen et al.¹²⁴ to (h) enhance the spectral response of perovskite-organic integrated devices and the resulting *J*-*V* curves. Reprinted with permission from Ref. 124. Copyright (2019) American Chemical Society.

Table 4. Summary of performance characteristics for perovskite/organic tandem photovoltaics. SPO indicates stabilised power output. *indicates values related to the integrated device concept.

Year	Configuration	V_{oc} (V)	J_{sc} (mAcm ⁻²)	FF	PCE (%) (SPO(%))	Ref
2015	Glass/ITO/PEDOT:PSS/PBSeDTEGS8:PCBM/PFN/TiO ₂ /PEDOT:PSS PH500/PEDOT:PSS 4083/MAPbI ₃ /PC ₆₁ BM/PFN/Al	1.52	10.05	67	10.2 (-)	¹⁰⁹
2015	Glass/ITO/TiO ₂ /MAPbI ₃ /DOR3T-TBDT:PC ₇₁ BM/MoO ₃ /Ag*	0.98	19.3	72.9	13.8 (-)	¹¹⁸
2016	Glass/ITO/PEDOT:PSS/PVSK/PC ₇₁ BM/PFN/Step layer/MoO ₃ /PBDTT-DPP/PCBM/Ca/Al	1.58	8.02	68	8.62 (-)	¹¹²
2016	Glass/ITO/PEDOT:PSS/Perovskite/PC ₆₁ BM/MoO ₃ /Ag/C60- SB/Polymer BHJ/C ₆₀ -N/Ag	1.62	12.9	76.1	15.9 (-)	¹¹³
2016	Glass/ITO/PEDOT:PSS/VO _x /Perovskite/PDPP2T:PC ₇₁ BM:N2200/ N-Doped TiO _x /Al*	1.06	20.04	77	16.36 (-)	¹²¹
2016	Glass/FTO/TiO ₂ /((FAPbI ₃) _{0.85} (MAPbBr ₃) _{0.15} /M3:PC ₇₁ BM/V ₂ O ₅ /Au*	1.095	22.2	71.5	17.3(-)	¹²²
2017	Glass/ITO/SnO ₂ /C ₆₀ /MAPbI ₃ /DPPEZnP-TSEH/PCBM/MoO ₃ /Ag*	1.03	23.32	78	19.02 (18.9)	¹⁰⁵
2018	Glass/FTO/TiO ₂ /MAPbI ₃ /PBDTT-E-T:IEICO/MoO ₃ /Ag*	0.993	24.08	60.97	14.57 (-)	¹²³
2019	Glass/ITO/SnO ₂ /CsPbI ₂ Br/PTAA/MoO ₃ /Au/ZnO/PTB7- Th:COi8DFIC:PC ₇₁ BM/MoO ₃ /Ag	1.71	11.98	73.4	15.04 (-)	¹¹⁵
2019	Glass/ITO/PTAA/((FAPbI ₃) _{0.85} (MAPbBr ₃) _{0.15} /Y6:PC ₇₁ BM:S1/ZrAcac /Ag*	1.1	22.75	78.4	19.62 (-)	¹²⁴

b) Other Perovskite based tandem concepts

Beyond the above-mentioned solution processed tandem architectures, there have also been other concepts reported that are not as widely investigated as those discussed above. For example, Karani et al.¹²⁵ investigated theoretically as well as experimentally the potential of coupling a MAPbI₃ perovskite absorber together with lead sulfide (PbS) colloidal quantum dots (CQDs) as the low bandgap absorber. They identified the possibility of achieving a PCE of 43% with a CQD absorber with $E_G = 1$ eV if radiative coupling between the two sub-cells are considered while a maximum PCE of 37% was identified to be possible with a CQD absorber with $E_G = 0.8$ eV. They further fabricated a tandem architecture consisting of PbS CQDs with $E_G = 1.03$ eV in combination with an MoO₃/ (Au or Ag) tunnel junction between the two sub-cells. However, a rather low PCE of 1.01% was reported.

An alternative to the use of 3D perovskite absorbers, processed based on the previously discussed routes, involve the use of perovskite quantum dots. While the initial performances of these quantum dots remained low (i.e. < 10%), developments on modification of quantum dot-quantum dot junctions¹²⁶ and ligand exchange for compositional stability¹²⁷ has enabled PCEs in excess of 16% for perovskite CQD PVs. Furthermore, the dimensionalities of such

CQDs also enables the formation of more stable inorganic perovskite absorbers to be fabricated¹²⁸ in comparison to the conventional synthesis routes reported where rapid degradation of the inorganic absorber is often observed. In this regard, Christians et al.¹²⁹ investigated the potential of utilizing CsPbI₃ CQDs for tandem architectures. However, a demonstration of perovskite CQDs have so far not been reported and remains an interesting area for future developments.

4. Approaches to manufacturability

4.1 Limitations of spin coated processing

Historically, spin coating has remained the preferred method for fabrication of small area, lab scale, solution processed photovoltaic technologies where substrate sizes typically do not exceed 2.5 cm x 2.5 cm. Indeed, in all the work discussed above, the fabrication of the perovskite absorber layer has relied on spin coating. Spin coating can be carried out via static or, dynamic dispensing where the ink is deposited on the substrate followed by the spin process in the former, whereas the ink is dispensed on an already spinning substrate in the latter. The resulting centrifugal forces results in a thin wet film. In situations where < 100 nm thick films are required, this often results in relatively dry films. On the other hand, during the fabrication of thicker films, the spin coating process often results in a semi-dry film which is often dried under thermal annealing to form the desired micro or nanostructure.¹³⁰

Fig. 7 Schematic illustrating (a) blade coating, (b) slot-die coating, (c) spray coating and (d) ink jet printing processes that are used for R2R and S2S fabrication of solution processed PVs.

For perovskites, spin coating has been the widely adopted methodology in terms of fabricating high-performing devices. In terms of single cation systems such as MAPbI₃, this often involves the careful control of the precursor composition (e.g.: the acetate route)^{114,131} and the ambient conditions (e.g.: the chloride route)^{4,132} which enables formulations that in principle can be adopted for scale-up coating techniques. However, in terms of the overall compositional space enabled by perovskites, the anti-solvent route¹³³ which enables a uniform nucleation and crystallization has been the more widely preferred methodology for perovskite fabrication. While the anti-solvent route was first implemented for MAPbI₃¹³³ to enable the fabrication of pin-hole free absorber layers, this was adopted early-on for the multi-cation⁷ systems which have demonstrated better stability, higher efficiency, and a larger processing window in glove box environments.

In industry (and specially the microelectronics industry), spin coating is somewhat implemented over wafer scales where wafer diameters approach 12". However, this often leads to a large wastage in terms of the solutions/inks used which is not attractive in terms of developing low-cost photovoltaic technologies. Furthermore, spin coating is somewhat restrictive in its throughput as it does not enable a high production rate that is targeted for low cost photovoltaic technologies. We do note however that there have been instances where the spin coating process has been used for the fabrication of lab scale modules with areas of ~100 cm².¹³⁴ Alternative technologies that enable the coating of perovskites and indeed, solution processed tandems include blade coating, slot die coating, spray coating and ink jet printing (Fig 7).

With regards to scaling up and manufacturability, Galagan et al.¹³⁵ highlighted the following key points which should be addressed to enable manufacturability of perovskites on a R2R or S2S system:

- 1) Solvent choice enabling control of viscosity, boiling point, toxicity, price.
- 2) Controlled crystallization enabling pin-hole free films.
- 3) Uniformity of layer properties.
- 4) Performance.

In achieving the above key goals, one of the critical points which require careful attention is the development of appropriate crystallization routes that can be implemented on a R2R or S2S system that will facilitate the formation of pinhole-free films.

4.2 Enabling compact pinhole free films

As indicated above, in the scaling up of perovskite coating process, one of the key challenges lies in the fabrication of a dense, pin hole free film. In this regard, the most attractive starting point in terms of forming a dense film is through the modification of the precursor composition. For example, while precursors consisting of PbI_2 and MAI is perhaps the most widely used for fabrication of MAPbI_3 , replacing PbI_2 with $\text{Pb}(\text{Ac})_2$ (lead acetate under the acetate route) has enabled compact-pin hole free perovskite solar cells to be formed¹¹⁴. Similarly, replacing PbI_2 entirely with PbCl_2 ⁴ in combination with appropriate control of ambient humidity¹³², or incorporating it with $\text{Pb}(\text{Ac})_2$ ¹³¹ also enables the formation of compact films.

An alternate route to enabling heterogenous nucleation in perovskites involves the deposition of the “semi-wet” perovskite film in a bath of the antisolvent¹³⁶ that is typically dripped during the anti-solvent based spin coating method. However, it has been highlighted that the processing window that enables the incorporation of the above is fairly limited in the conventionally used DMF: DMSO solvent mixtures. This led Yang et al.¹³⁶ to modify the original solvents used in the perovskite precursor to incorporate 1-methyl-2-pyrrolidone (NMP) which slowed down the drying dynamics enabling an anti-solvent bath to be used to enable heterogenous nucleation and crystallization to proceed.

From an overall scaling point-of-view, it would still be attractive to eliminate the need for an anti-solvent step. One potential route towards achieving this is through coating of the material on a heated substrate.^{137,138} Additionally, the use of acetates or chlorides highlighted above, the incorporation of additives into the precursor is an attractive route towards enabling compact films. This has already enabled the demonstration of modules incorporating additives¹³⁹ such as didodecyldimethylammonium bromide, polyethylene glycol sorbitan monostearate, sodium dodecyl sulphate. Additionally, gas quenching methodology^{136,140} which was first implemented for spin coating methods in place of anti-solvent treatment is a route that enables the homogenous nucleation during R2R or S2S coating of perovskites. In this process, the blowing of a gas (often N_2) results in speeding up of the (precursor) solvent evaporation that leads to in rapid saturation and precipitation of nucleation species which enables the formation of a dense pin-hole free film. This technique has already been adapted in R2R and S2S coating techniques for perovskite where the use of an air-knife¹⁴¹ facilitates the desired saturation, precipitation and crystallisation to take place, enabling dense films.

4.3 Large area coating methods

In terms of high throughput R2R and S2S manufacturing, we now outline some of the most promising routes. A summary of advantages and disadvantages of each technique are also indicated in Table 5. We note that the details given above are not exhaustive and the readers are referred to more detailed reviews discussing individual techniques and the references therein.^{142–147}

Table 5 Comparison of advantages and disadvantages of the large area coating techniques discussed in this review.

Technique	Advantages	Disadvantages
Blade coating	<ul style="list-style-type: none">• Can be used for both lab scale optimization and industrial manufacturing.• Significant reduction in ink used compared to spin coating as well as slot die coating.	<ul style="list-style-type: none">• More appropriate for S2S printing as opposed to R2R printing.
Slot-die coating	<ul style="list-style-type: none">• Appropriate for high throughput manufacturing on a R2R system.• Can also be used for pilot scale optimization studies for S2S printing.• Better yield and reproducibility compared to blade coating.	<ul style="list-style-type: none">• Not suited for optimization of inks due to high usage for a single print.
Spray coating	<ul style="list-style-type: none">• Can be used for both lab scale optimization and industrial manufacturing.	<ul style="list-style-type: none">• Careful optimization of ink required to avoid clogging of spray head.• Low throughput compared to blade coating and slot-die coating.
Inkjet printing	<ul style="list-style-type: none">• Can be used for both lab scale optimization and industrial manufacturing.• Better control in terms of feature sizes enabling the removal of additional laser scribing steps for material removal.	<ul style="list-style-type: none">• Clogging of print head can cause disruptions requiring careful optimization of ink and appropriate maintenance of head.• Low throughput compared to blade coating and slot die coating.

a) Blade coating

Blade coating has been a relatively widely used technique in S2S coating manufacturing. In simple terms, this technique involves the use of a blade for the spreading of the ink on the substrate (Fig. 8(a)). Appropriate control of the speed of the blade, the substrate-blade gap, the concentration and viscosity of the ink enables the formation of a wet film, that is subsequently dried to form the final film. This not only results in a very low ink usage, but also enables the fabrication of lab scale devices as well as large scale modules, enabling scalability in terms of the ink composition and drying methodologies used. While difficulty in patterning can be

pointed out as a potential disadvantage for this technique, this is less likely to be relevant for printed solar cells where laser scribing processes are used for the patterning required which often is in the millimeter length scales.

Blade coating has been a widely used technique in organic photovoltaics in terms of developing small area devices¹⁴⁸ as well as for demonstrating scaling up of printed photovoltaics^{29,149}. However, as discussed previously, appropriate modifications need to be implemented either to the precursor, or the coating process to enable the formation of a compact film.

Among the methodologies utilized for obtaining a compact absorber layer based on perovskites, through blade coating has involved the use of substrate heating as means of both solvent removal as well as initiation of perovskite crystallisation. For example, Wu et al.¹⁵⁰ reported a module efficiency of ~11% achieved through blade coating of a precursor mixture consisting of MAI and PbI₂ in DMF on a heated substrate (temperature varied from 60 – 160° C) which resulted in a PCE of ~11%. This work was subsequently modified by Peng et al.¹⁵¹ where the solvent used in the precursor was modified to a DMF:DMSO solvent mix and through the incorporation of excess MAI which enabled the formation of a more optimized absorber resulting in an average PCE of 10.16% (champion PCE of 10.92%) for an aperture area of 0.09 cm².

With regards to the impact of the substrate temperature on the formation of perovskites during blade coating, Zhong et al.¹⁵² reported insights on the crystallisation dynamics of perovskites under different substrate temperatures based on in-situ grazing incidence wide-angle X-ray scattering (GIWAXS) studies (Fig. 8(a)-(d)). For a precursor solution consisting of MAI and PbI₂ in DMF, they observed the formation of a highly disordered and heavily solvated film for periods exceeding 200 s when the precursor is blade coated at room temperature. Increasing the substrate temperature resulted in a faster transition from the highly disordered and solvated film condition to a more ordered condition. For example, at 80° C, this transition was observed to take place at ~13s. When the temperature was further increased, the time for this transition was even further reduced (e.g. to ~2.4 s at 135° C). The resulting device performances also demonstrated a strong correlation to the transition from the highly disordered state to a more ordered state where the PCE increased with increasing substrate temperature.

Li et al.¹⁵³ utilised a combination of solvents in the precursor and investigated the impact of the blade coating temperature on the conversion of the precursors in forming the final perovskite absorber layer. For a solvent mixture of DMSO: gamma Butyrolactone (GBL),

studies on the film formation based on GIWAXS when blade coated at room temperature was observed to follow a similar route to that of spin coated samples without an anti-solvent. However, due to the slow solvent drying process, the resulting film formation also proceeded at longer time scales which is not an attractive feature in terms of high-throughput manufacturing. However, when the blade coating temperature was increased to 150° C, a direct transition from the disordered sol-gel phase to the crystalline phase was observed, enabling higher film quality. Optimization of the above conditions enabled a champion PCE in excess of 18% for devices with an active area of 0.09 cm² while a PCE of 17.06% was observed for 1 cm² cells. In addition to the above, the blade coating speed has a significant impact on the formation of compact films. For example He et al.¹⁵⁴ reported high efficiencies of 19.81% for (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15} over active areas of 0.1 cm² and 18.02 cm² for aperture areas of 0.98 cm² by employing a slow coating speed in combination with high boiling point solvents. However, the use of slow coating speeds is less preferable in terms of high production rates. At higher blade coating speeds (>20 mms⁻¹), Deng et al.¹³⁹ noted the need for a surfactant that would minimize microscale fluid flows that results in the formation of islands (Fig. 8(e)). In their work surfactants such as didodecyldimethylammonium bromide, polyethylene glycol sorbitan monostearate, sodium dodecyl sulphate were incorporated into the MAPbI₃ perovskite precursor which enabled the formation of a dense film at high coating speeds of 50 mms⁻¹. This enabled PCEs of 20.3% for small area cells (0.075 cm²) and 14.6% for a module with an aperture area of 57.2 cm² (Fig. 8(f) and (g)). It should be noted that in the case of forming a dense perovskite film, the hydrophilic/hydrophobic nature of the underlying layer also plays a critical role. For example, modification of PEDOT:PSS used as an HTL in blade coated devices by incorporating poly(4-styrenesulfonic acid) into the mixture was reported to enable scalable coating of MAPbI₃ based on using PbCl₂ as the Pb²⁺ source, resulting in an average PCE of 8.29% and a champion PCE of 10.15%. It is noted that in the case of the above, the authors utilized DIO in perovskite precursors as well as a high coating speed between 2.5 – 10 cms⁻¹, although substrate heating was not used.

Beyond the more widely adopted approaches discussed above, we note that increasing the processing window (Fig. 8(h)) to enable anti-solvent bath deposition as a means of uniform crystallization has been reported for blade coated samples. For example, Yang et al.¹³⁶ utilised a solvent mix of DMF and NMP which enabled the blade coating of perovskite precursors consisting of MAI, PbI₂ and PbCl₂ followed by dipping in a bath of diethyl ether. This enabled stabilized efficiencies >19% for 0.12 cm² cells while a PCE of >17% was achieved for 1.2 cm²

cells. The technique was further extended to a small area module with an active area of 11.09 cm² which resulted in a PCE of 13.3% (Fig. 8(i) and (j)). We note that somewhat of a similar approach was adopted by Eperon et al.⁹⁰ in fabricating the low band gap Pb-Sn mixed absorber, although the film was fabricated through spin coating. However, careful control as well as optimization of the humidity and temperature is important depending on the precursor used (e.g. PbCl₂ in the perovskite precursor mix) as has been demonstrated for spin coated¹³² as well as blade coated¹⁵⁵ PSCs.

Fig. 8 Time dependent GIWAXS scans of (a) spin coated, and blade coated perovskite layers where the substrate was held at (b) 25° C (c) 80° C and (d) 135° C as reported by Zhong et al.¹⁵² Reprinted with permission from Ref. 152. Copyright (2018) American Chemical Society. (e) The influence of surfactants on the surface coverage of blade coated perovskites and the resulting (f) small area device and (g) module performance as reported by Deng et al.¹³⁹ Reproduced from Ref. 139 with permission from Springer Nature. (h) The influence of solvent composition on the processing window which enables anti-solvent bath treatment of films coated using scalable techniques resulting in (i) smooth, compact films. (j) The resulting J - V characteristics for a film with an active area of 1.2 cm² which enables a PCE > 17%.¹³⁶ Reproduced from Ref. 136 with permission from Springer Nature.

b) Slot-die coating

Slot-die coating can be considered as being somewhat similar to the blade coating method discussed above, with the exception of a continuous ink flow which enables R2R coating as opposed to S2S coating (only). A reservoir containing the ink is fed to the slot-die head which is applied to the substrates through a thin slit (shim) (Fig. 7(b)). The ink viscosity, precursor concentration¹⁵⁶, relative speed between the blade and the substrate is used to control the thickness of the final film while a heated bed is often preferred to enable uniform drying on a macroscopic scale. Slot die coating is a technique that has been widely adopted in the field of organic photovoltaic development activities focusing on high throughput R2R manufacturing^{157–159}.

As per the case of blade coating of perovskites, precursor solutions can be coated at either room temperature or on substrates held at elevated temperatures, while an air knife can be used in order to control the crystallization during the coating process (Fig. 9(a)), enabling R2R fabrication on flexible substrates (Fig. 9(b)). Furthermore, this technique is compatible with either the single-step (where all the components of the perovskite are mixed in a single precursor) or the two-step (where the lead precursors and the organohalide precursors are prepared in separate solvents and are sequentially coated) process. For example, Qin et al.¹⁶⁰ utilized a two-step process involving the slot die coating of PbI_2 in DMF at temperatures between 25 – 30° C followed by dipping the coated substrate in a bath of MAI. The work resulted in PCEs of 11.7% and 14.75% over active areas of 0.1 cm² for devices with slot die coated Spiro-OMeTAD and 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenyl)amine-9,9'-bifluorenylidene (Bifluo-OMeTAD) respectively.

In comparison to the 2-step approach, the single step coating is perhaps more favoured, especially in terms of potentially reducing the processing time on a R2R manufacturing process. For example, Cotella et al.¹⁴¹ adopted a single step coating process for a perovskite based on MAI and PbCl_2 in DMF. The precursor was coated on preheated substrates held at 20, 65 or 90° C which were achieved by placing the substrate in an oven for 30 min prior to coating. The optimum coverage was observed following preheating at 65° C while combining this with a cold air knife has enabled the formation of a smoother film. Devices optimized in this manner resulted an average PCE of 7% and a champion PCE of 9.2% for an aperture area of 0.0625 cm². A similar approach was reported by Ciro et al.¹⁶¹ who reported the fabrication of flexible perovskite solar cells through coating of a precursor mix similar to that used by Cotella et al.¹⁴¹ on a heated ITO/polyethylene terephthalate (PET) substrate. The formation of a compact perovskite film was observed to depend on both the substrate temperature as well as

the precursor concentration; an increased concentration at low temperatures results in the reduction of pinhole formation while increasing the temperature at all concentrations studied enabled the formation of compact films. Following further optimization for the PC₆₁BM coating (used as the electron transport layer) thickness, a champion PCE of 2.91% was achieved.

Giacomo¹⁶² et al. used a modified precursor consisting of PbCl₂ and Pb(Ac)₂ as the lead sources and MAI in DMF for coating over 6" × 6" substrates (Fig. 9(c)-(e)). For devices with an active area of 0.09 cm² tested with an aperture area of 0.04 cm², an average PCE of 16.4% was achieved. Lee¹⁶³ et al. utilized a similar precursor mix as that of Giacomo et al.¹⁶², but studied the influence of the ratio between the Pb²⁺ sources. A gas blowing method was implemented while the slot die coating was carried out under ambient temperature. The authors focused on the lower end of PbCl₂ loading as the increase in PbCl₂ results in longer annealing times. The incorporation of PbCl₂ was noted to be beneficial in terms of increasing the perovskite grain sizes. In terms of devices, a champion PCE of 13.3% was reported for Pb(Ac)₂: PbCl₂ of 8:2. The use of both lead sources enabled pinhole free film formation as opposed to Pb(Ac)₂ only. In order to demonstrate the possibility of scaling up, the authors investigated the performance of a module with an area of 10 cm² which enabled a champion PCE of 8.3%.

Kim¹⁶⁴ et al. combined the gas blowing technique and substrate heating to improve slot die coated device performance. The absence of heating on the precursor consisting of MAI: PbI₂ mix in DMF resulted in needle like structure formation with gas blowing only, while incorporation of substrate heating enabled more dense film formation. The authors also investigated the incorporation of additives DMSO, ammonium chloride (NH₄Cl) and N-cyclohexyl-2-pyrrolidone (CHP) where the latter two enabled better film quality for slot die coated films. The authors evaluated the use of P3HT and Bifluo-OMeTAD as HTLs in combination with different substrate heating temperatures for the perovskites where the best performance was observed for Bifluo-OMeTAD resulting in a champion PCE of 12.73%. The latter aspect also indicates the importance of optimization of the transport layer materials to improve PCE for printed PSCs.

In terms of manufacturing, there is a strong need towards the elimination of toxic solvents such as DMF as highlighted by Galagan et al.¹³⁵ In their work, a solvent mix consisting of DMSO and 2-butoxyethanol (2BE) was utilised where the latter solvent enabled better wetting of the precursor, formation of a uniform perovskite layer and acceleration of crystallization. When evaluated using precursors based on MAI and PbI₂, needle-like structures were obtained when a slow heat up ramp was following the slot die coating process while a mixture of plate-like

large crystals and some needle-like features were obtained when the temperature ramping rate was increased. To obtain better crystallization, the perovskite composition was changed to $\text{Cs}_{0.15}\text{FA}_{0.85}\text{PbI}_{2.85}\text{Br}_{0.15}$. Using the same solvent composition as above, plate-like structures were obtained under slow, as well as the fast temperature ramping rates (following the precursor coating) which enabled PCEs of 15.2% to be obtained for active areas of 0.09 cm^2 on an ITO/PET substrate (Fig. 9(f) and (g)). When a similar device was fabricated using DMF as the solvent on glass using spin coating, a PCE of 15.8% was obtained while 13.5% was obtained for the DMSO:2BE solvent mix. This difference in performance between the spin coated samples and the slot die coated samples was attributed to the sheet resistance of the ITO used in terms of slot die coating where PET/ITO was used.

Fig. 9 (a) Schematic illustrating the air knife method employed during slot die coating of perovskites. (b) A R2R slot die coating system with a printed, flexible PSC shown on the inset.¹³⁵ Reproduced from Ref. 135 with permission from Wiley-VCH. (c) PCE homogeneity mapping of slot die coated PSCs reported by Giacomo et al.¹⁶² over a $6'' \times 6''$ area and (d) a photograph of such a printed module. The resulting *current-voltage* and *power* curve are given in (e). Reproduced from Ref. 162 with permission from Elsevier B.V. (f) *J-V* and (g) MPP, *current density* and *voltage* at MPP tracking for flexible PSCs printed using less toxic solvents as reported by Galagan et al.¹³⁵ Reproduced from Ref. 135 with permission from Wiley-VCH.

c) Spray coating

Spray coating is another technique that can be used for the scaling up of perovskite photovoltaic coatings for R2R or S2S fabrication. Under the spray coating method, a pressurized gas system or an ultrasound head is used to break down the precursor into droplets which are deposited on the substrate (Fig. 7(c)) which can be either heated or at room temperature.¹⁶⁵ The resulting semi-dry films can then be further processed either under vacuum¹⁶⁶, in a solvent bath¹⁶⁷ followed by thermal annealing^{168,169} to enable the formation of the final layer.

In terms of spray coated perovskite devices, one of the earliest reported work was by Barrows et al.¹⁶⁹ who used ultrasonic spray coating to deposit $\text{MAPbI}_{1-x}\text{Cl}_x$. The coverage of the perovskite layer was observed to be dependent on the substrate temperature where $\sim 85 \pm 5\%$ coverage was achieved at a substrate temperature of 75°C . Furthermore, the authors reported that a lower post annealing processes required a long crystallization time while annealing temperatures above 110°C resulted in a de-wetting effect (Fig. 10(a)-(f)). An average thickness of $\sim 340\text{ nm}$ was observed to be ideal for the spray coated perovskite solar cell performance resulting in an average PCE of 7.8% and a champion PCE of 11.1%. Das et al.¹⁷⁰ reported the use of ultrasonic spray coating of precursors based on MAI and PbCl_2 in DMF, on glass and ITO/PET substrates. Substrate heating was employed to enable rapid drying of the films. The authors reported an optimum substrate temperature of $\sim 75^\circ\text{C}$, similar to that reported by Barrows et al. Devices fabricated on glass substrates resulted in a champion PCE of $11.4 \pm 0.4\%$. Following this, the authors translated the process to a flexible ITO/PET substrate where high density infrared pulses were used to cure the TiO_2 layer which resulted in a significantly poor performance of 0.4%.

Mohamad et al.¹⁶⁸ demonstrated a spray coated perovskite solar cell based on $\text{MAPbI}_{1-x}\text{Cl}_x$ where the HTL and ETL (PEDOT:PSS and PCBM) were also spray coated resulting in an average PCE of 7.1% and champion PCE of 9.9% over an aperture area of 0.025 cm^2 while cells where only the perovskite absorber was spray coated enabled an average PCE of 9.8% and a champion PCE of 11.1%. Also, humidity was observed to have an impact on the performance where an increase in the humidity leading to a reduction of PCE.

Heo et al.¹⁷¹ developed a unique approach for spray coating of perovskite films by balancing out the outgoing solvent flux with the sprayed perovskite precursor enabling a longer spray coating window. MAI and PbCl_2 were first reacted in IPA which were then purified and dissolved in a DMF/GBL solvent mix. Balancing of the DMF:GBL ratio was identified to be crucial in enabling the balancing of the solvent flux out with the spray coated precursor mix.

This resulted in spray coated cells with a PCE of 18.03% over 0.16 cm². They further demonstrated the possibility of fabricating a spray coated module with an active area of 40 cm² resulting in a PCE of 15.5%.

Bishop et al.¹⁴² modified the previously mentioned process reported by Mohamed et al.¹⁶⁸ to enable spray coating of the compact TiO₂, mp-TiO₂, the MAPbI_{1-x}Cl_x absorber and spiro-OMeTAD. Hydroiodic acid was used as an additive to enable better solubility of PbCl₂ in DMF while also promoting better surface coverage. The work enabled an average PCE of 9.2% over a 4 mm² pixel (aperture area of 0.0256 cm²) while cells with an active area of 1.51 cm² enabled an average PCE of 6.59 cm² (Fig. 10(f)-(h)).

An alternate route towards the fabrication of perovskite absorbers is based on the 2-step method.^{172,173} For example, Huang et al.¹⁷³ developed a 2-step spray coating process to fabricate MAPbI₃ based solar cells. Initially, PbI₂ in DMF was spray coated followed by spray coating of MAI in 2-propanol (IPA). The temperature was identified to be a key parameter as too-high temperature(s) did not enable the infiltration of the MAI into the dense PbI₂ layer while a too-low temperature resulted in residual DMSO. The optimized coating process resulted in a PCE of 13.09% for a 1 cm² pixel.

In comparison to the organic-inorganic hybrid perovskite spray coating reported as in the above work, Lau et al.¹⁷⁴ developed spray coated all inorganic perovskite solar cells, an important composition in terms of forming thermally stable perovskites.¹¹⁶ In that work, a “semi” spray coated method was adopted where CsI was spray coated on a spin coated PbBr₂ film enabling the formation of an all inorganic perovskite absorber. The substrate temperature was identified to have a crucial impact on the perovskite formation with substrates kept at room temperature enabling the desired perovskite phase while heating of the substrate to either 160° C or 350° C resulted in the formation of an undesirable CsI phase. A best PCE of 5.4% was achieved for the room temperature spray coated samples while PCE <3% was achieved for those prepared using heated substrates.

The use of spray coating also enabled the development of rapid compositional screening. For example, Tait et al.¹⁷⁵ utilised concurrent spray coating of mixtures of PbCl₂: MAI and Pb(Ac)₂: MAI in DMF on substrates held at a temperature of 40 – 60° C (40° C being identified as the optimum). Based on the above method, the optimum PbCl₂: Pb(Ac)₂ ratio was identified to be 3:1 which facilitated low pinhole formation as well as good photovoltaic device performance resulting in a PCE of 13.7% for device areas of 0.13 cm² and a PCE of 10.4% for module areas of 3.8 cm². The authors also investigated concurrent spray coating of PbCl₂: MAI and PbBr₂:

MABr to enable bandgap tuning which resulted in a PCE of 6.8% for perovskite with an E_{BG} of 1.8 eV. A more traditional approach towards compositional screening was reported by Chou et al.¹⁷⁶ who reported the spray coating of $MA_{1-x}FA_xPbI_3$ where $x = 0, 0.25, 0.50, 0.75$ & 1 was investigated. The optimum performance was realized for $x = 0.25$ which resulted in a champion PCE of 15.61% when the precursor was spray coated on a heated substrate kept at 70° C. The work highlights the role of spray coating techniques as means of compositional optimization of perovskites, an area that is receiving significant attention in terms of utilizing machine learning approaches.^{177,178}

Cai et al.¹⁷⁹ utilised hot air blowing during the fabrication of spray coated cells. In their work, this methodology was reported to result in better reproducibility of $MAPbI_{1-x}Cl_x$ (in DMF) based PSCs resulting in a PCE of 13.5% (reverse scan) for an aperture area of 0.13 cm² and 9.8% for an active area of 1 cm².

With regards to the drying of the spray coated films, an alternate approach to the conventionally used thermal annealing process involves the vacuum drying of the spray coated samples that is followed by thermal annealing¹⁶⁶, analogous to VASP reported by Bi et al.⁵¹ Based on this approach, Bishop et al.¹⁶⁶ spray coated the triple cation perovskite; $Cs_{0.05}[(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}]_{0.95}$ in a DMF:DMSO = 4:1 solvent mix onto a substrate held at 40° C followed by a vacuum drying and subsequent thermal annealing process which enabled a higher V_{OC} compared to samples that have not undergone the vacuum drying process. The resulting devices showed an average PCE of 17.8% in the reverse direction with more spatially homogenous optoelectronic characteristics compared to non-vacuum dried films (Fig. 10(i)-(k)).

Fig. 10 Optical microscopy images of spray coated films on heated substrates held at (a) 28° C, (b) 38° C, (c) 55° C, (d) 75° C, (e) 80° C and (f) 87° C indicating the importance of temperature control for compact perovskite absorber formation as reported by Barrows et al.¹⁶⁹ The scale bar corresponds to 20 μm. Reproduced from Ref. 169 with permission from The Royal Society of Chemistry. (g) Photographs of small area and (h) large area spray coated MAPbI₃ solar cells reported by Bishop et al.¹⁴² where the compact and mp-TiO₂ were also spray coated in addition to the perovskite absorber. (i) The topographical (top row) and light beam induced current (LBIC) maps (bottom row) where in device A: all layers are spin coated, device B: only the mp-TiO₂ is spray coated, device C: only the perovskite absorber is spray coated, device D: both the mp-TiO₂ and the perovskite spray coated and device E: all of the above layers are spray coated.¹⁴² Reproduced from Ref. 142 under the Creative Commons CC BY License. LBIC maps of (j) non-VASP and (k) VASP processed, spray coated triple cation PSCs. Reported by Bishop et al.¹⁶⁶ (l) Shows the *J-V* characteristics of a spray coated, VASP processed triple cation PSC. Reprinted with permission from Ref. 166. Copyright (2018) American Chemical Society.

d) Ink jet printing

In terms of printed solar cells, ink jet printing is another attractive technology that bridges the gap between lab scale evaluation and manufacturing through R2R or S2S processes. In-fact, perovskite based solar cells fabricated through ink-jet printing (Fig. 7(d)) are already being evaluated as window facades.¹⁸⁰ Ink jet printing and drop-on-demand printing¹⁴⁶ (Fig. 11(a) and (b)). In continuous printing, the ink is forced through a nozzle where it results in a column of droplets due to the surface tension. The droplets then pass through a nozzle where a charge is imparted on it. The direction of printing is steered by deflection plates which steer the direction of the droplets. In the drop-on-demand printing method, a pressure pulse is generated in the head either through a piezoelectric transducer or through rapid heating of the ink which results in the formation of a bubble at the surface of a heater. The resulting pressure pulse drives the ink through the nozzle resulting in the refilling of the ink. It is noted here that ink jet printing has so far produced some of the best performing large area perovskite modules with the collaboration between Panasonic and Japan's New Energy and Industrial Technology Development Organization (NEDO) reporting²⁵ a PCE of 16.09% for an aperture area of 802 cm² (Fig 11(c)) while Saule Technologies, a company that is developing ink jet printed perovskite solar cells has tested a module on Skanska's Spark office in Warsaw¹⁸¹.

As in the case with many other manufacturing techniques, in inkjet printing of perovskites also, the substrate temperature plays a key role in terms of forming a compact perovskite film. For example, Li et al.¹⁸² demonstrated the inkjet printing of a perovskite layer consisting of MAI:PbI₂:MACl = 1-x:1:x in GBL where substrate heating was implemented to enable rapid ramping of the temperature from 25° C to as high as 60° C within a couple of minutes which was identified to facilitate homogenous crystallization, similar to that of anti-solvent treatment^{8,11,12,133} and hot casting techniques^{137,138}. A temperature of 50° C together with MAI:MACl ratio of 4: 6 (i.e. $x = 0.6$) was identified as being the optimum condition to achieve the best performance of 12.3% where the MACl was identified to result in homogenous crystallization of the perovskite.

Mathies et al.¹⁸³ utilised inkjet printing for the coating of MAPbI₃ based on a solvent system consisting of DMSO and GBL which enabled slow solvent evaporation, and thereby resulting in the formation of smooth, thin films. Optimum performances were observed to be obtained following the incorporation of a vacuum annealing step over a duration of 2 or 5 min, which resulted in the best performances of ~4.5% and 4.3% for a single coating (i.e. perovskite thickness of ~180 nm). However, the performance was observed to decrease if the vacuum

annealing was carried out for shorter or longer periods. Applying three coatings to enable a thickness of ~480 nm in combination with vacuum annealing resulted in a higher PCE of 11.3% for a device area of 0.09 cm² (Fig. 11(d)-(f)). Following this initial work on MAPbI₃¹⁸³, Mathies et al. reported¹⁸⁴ the use of a triple cation perovskite, C_{0.10}(FA_{0.83}MA_{0.17})_{0.90}Pb(I_{0.83}Br_{0.17})₃ in combination with the vacuum annealing process optimized at 2 min. The drop spacing was altered from 60 μm to 25 μm enabling the increase in thickness from 180 nm to 780 nm. A champion PCE of 15.3% (Fig 11(g)) was obtained for a thickness of 520 nm. The triple cation printed devices also demonstrated an improved thermal stability compared to MAPbI₃ with only 10% loss in PCE when kept at 80° C for 100 min.

Liang et al.¹⁸⁵ reported the printing of MAPbI₃ precursors prepared in a DMSO: GBL mix to print perovskite films in combination with vacuum annealing. They achieved PCEs of 17.04% for 0.04 cm² and 13.27% for 4 cm². The improvements in performance was enabled by deposition of a 5 nm thick C₆₀ layer on the TiO₂ ETL where the C₆₀ coating enabled larger grains to be formed as well as an increased recombination resistance.

Gheno et al.¹⁸⁶ evaluated the importance of the halide composition on methylammonium based perovskites in conjunction with the impact of printing on metal oxide films (TiO₂ compact or mesoporous films (mp-TiO₂), or tungsten oxide (WO_x) films). Four perovskite compositions were evaluated: MAPbI₃, MAPbI_{3-x}Cl_x, MAPbI_{3-x}Cl_x with DIO as an additive and MAPbI_{3-x}Br_x. ITO substrates stored in air enabled a more hydrophilic surface for printing of the MAPbI_{3-x}Cl_x while WO_x in nitrogen enables a similar outcome. This work enabled the identification of the importance of controlling the overall perovskite concentration such that the jetability is not impacted was identified, although it should be noted that it is likely that additives such as 5-ammonium valeric acid iodide (5-AVAI) would also reduce the clogging of the printing head as reported by Hashmi et al.¹⁸⁷ The influence on jetability is most likely due to presence of colloids in the perovskite precursors.¹⁸⁸ The authors printed tungsten oxide (WO_x) as an ETL/perovskite/Spiro-OMeTAD and evaluated solar cell performance. A champion PCE of 10.7% was achieved in reverse scan, although a large hysteresis was also observed.

Huckaba et al.¹⁸⁹ reported inkjet printed PSCs where both the perovskite as well as the mp-TiO₂ were inkjet printed. In order to minimize the coffee-ring effect when drying, a solvent combination of DMF/DMSO/GBL/NMP was used together with phosphatidylcholine as a surfactant. The perovskite composition followed a quadruple cation system based on: Cs_{0.10}Gu_{0.05}(FA_{0.83}MA_{0.17})_{0.85}PbI_{2.63}Br_{0.37}. Contrary to the above conditions, the authors dipped

the coated film in an anti-solvent bath of diethyl ether to enable homogenous crystallization. Decreasing the drop spacing during inkjet printing enabled the formation of a compact film as well as thicker film to be formed. A champion PCE of 14.1% was obtained with an average cell efficiency of 12.15% for devices with an area of 0.16 cm² which was much higher than that obtained for inkjet printed MAPbI₃ cells.

Hashmi et al.¹⁸⁷ utilised inkjet printing towards fabrication of the perovskite absorber and the insulating ZrO₂ spacer layer on a porous carbon layer to fabricate HTL free solar cells (Fig. 11(h)). The precursor used consisted of a mix of MAPbI₃ and 5-AVAI mix which has previously been reported¹⁹⁰ to result in one of the most stable device architectures. While 5-AVAI enables slow crystallization, it also prevents the clogging of the inkjet head, enabling optimized devices with PCEs of 8.47% (in the reverse for an aperture area of 0.16 cm²) to be achieved. Initial investigations on the device stability where the cells were kept under illumination at 35° C for 1046 h showed very little decrease in performance. When stored in the dark for 3 weeks, the performance was observed to improve by 13% to a value of 9.53% for the champion cell (Fig. 11(i)). This work was later expanded¹⁹¹ to identify the stability of the cells under UV irradiation where the devices, when encapsulated with an epoxy showed no performance degradation under UV irradiation equivalent to 1.5 Sun illumination conditions over 1002 hours.

An interesting approach in terms of “colouring” of perovskite solar cells was reported by Schliske et al.¹⁹² who incorporated ink jet printed luminescent down shifting layers (mixtures of Violet 570, Yellow 083, and Red 300 Lumogen-F series, BASF in polymethylmethacrylate) together with a solar cell consisting of ink-jet printed perovskite layer Cs_{0.10}(FA_{0.83}MA_{0.17})_{0.90}Pb(I_{0.83}Br_{0.17})₃. However, the PCE was observed to decrease from 11.5% to 9.4% following the incorporation of the down-shifting layers. Such an approach is likely to be attractive in terms of developing perovskites for building integrated PV where variation in colours is preferred for aesthetic purposes.

The use of inkjet printing has also been used rapid compositional screening of perovskites. For example, Bag et al.¹⁹³ used in-situ mixing capabilities of multichannel ink-jet printers to explore the compositional space based performance of ink-jet printed perovskite solar cells where the CMYK (cyan magenta yellow black) channels consisted of MA⁺, FA⁺, water, water. By variation of the CMYK values, different MA:FA combinations was evaluated. The resulting printed devices indicated the best performance to be obtained from an MA:FA = 2:1 resulting

in a champion device performance of 11.1%. As noted previously for similar activities discussed under spray coating, inkjet printed compositional screening provides an avenue that support machine learning based perovskite composition optimization activities.

is based on 2 approaches: continuous printing

Fig. 11 Inkjet printing based on (a) continuous and (b) drop-on-demand technique. (Schematic based on ref¹⁴⁶). (c) Photograph of 30 cm $\times$ 30 cm inkjet printed perovskite module by Panasonic.¹⁹⁴ Photograph reproduced with permission from Panasonic. Light beam induced current mapping of inkjet printed (d) non-vacuum treated, (e) vacuum treated and (f) spin coated perovskite films reported by Mathies et al.¹⁸³ Reproduced from Ref. 183 with permission from The Royal Society of Chemistry. (g) $J-V$ characteristics of inkjet printed triple cation perovskites of varying thickness (from 150 nm – 750 nm) reported by Mathies et al.¹⁸⁴ Reprinted with permission from Ref. 184. Copyright (2018) American Chemical Society. (h) Process steps followed by Hashmi et al.¹⁸⁷ in fabricating inkjet infiltrated carbon porous contact based PSC and, (i) the improvement in performance of these devices following storage in the dark for 3 weeks. Reproduced from Ref. 187 with permission from Wiley-VCH.

5. Prospects and future directions

One of the key issues in the development of perovskite absorbers has been its inherent instability under certain compositions. For example, MAPbI₃, the fruit-fly of perovskite research has been identified to demonstrate inherent instability under elevated temperatures (>85° C) condition. MAPbI₃ often requires annealing temperatures closer to 100° C, there is the need towards screening for compositions which minimise or eliminate this risk.

As discussed in this review, one of the key attractions in the development of PSCs has been its bandgap tunability, which enables the formation of low bandgap absorbers based on Pb-Sn mixed perovskites. However, the oxidation of Sn²⁺ (the preferred oxidation state for PSCs) to Sn⁴⁺ remains a key challenge, especially considering that it would be preferable to carry out the printing of low bandgap perovskites under ambient conditions, which accelerates the oxidation of Sn²⁺. In terms of minimising oxidation, A number of routes have been developed such as the inclusion of SnF₂¹⁹⁵, use of appropriate anti-solvent washing such as toluene (Fig. 12(a)) and annealing temperatures¹¹ as well as the inclusion of tin powder¹² (Fig. 12(b)) to the precursor mix. In terms of a R2R or S2S printing capability, we do not foresee any significant barrier towards utilising the above methodologies. However, more in-depth studies are required in this regard to ensure that stable, low bandgap absorbers can indeed be printed on high throughput manufacturing systems.

Another significant impediment towards the high throughput manufacturing of perovskite based tandem structures is the use of toxic solvents such as DMF, chlorobenzene (CB), dichlorobenzene (DCB) etc.^{7,10,12}. For example, solvents such as DMF is noted for its harmful nature (when in contact with skin)¹⁹⁶. Similar obstacles have been highlighted in the manufacturing of organic photovoltaics which use solvents such as CB or DCB in lab scale device optimization. This has in fact resulted in studies for the optimization of this technology based on green solvents^{197,198}. With regards to perovskites, there have been demonstrations towards the development of precursors based on more environmentally friendly solvents. For example, Gardner et al.¹⁹⁹ has discussed several environmentally friendly solvent combinations for the perovskite precursor while Galagan et al.¹³⁵ have demonstrated slot die coated examples of perovskites where DMF has been eliminated. Noel et al.²⁰⁰ (Fig. 12(c)) has also reported clean, low boiling point solvents that can enable the fabrication of perovskites in a manner that can be implemented on a manufacturing line. This approach was more recently reported²⁰¹ to be utilised for the development of slot die coating in conjunction with an air knife for the

fabrication of perovskites on ITO/PET which demonstrated a champion PCE of 14.7%. However, there remains significant room for further improvement that will require future activities at lab scale processes to focus on the uptake of environmentally friendly manufacturing methodologies to ensure that the promise of perovskites as a printed PV technology is realised.

In terms of future applications beyond contribution to the grid, it is anticipated that perovskites will be integrated into building components with early developments already being reported. While a current limitation lies in terms of its aesthetics (i.e. colour of the module), the approach reported by Schlisske et al.¹⁹² is likely to enable this issue to be bypassed. Other than this, perovskite-based tandems are also likely to lead to space-based energy harvesting applications. The reported high radiation tolerance is likely to make this technology a favourable candidate. This could also be considered as a new application space for all-perovskite tandem solar cell applications where module degradation due to oxygen and moisture are of less concern. Additionally, the satisfactory performance of perovskites under concentrator applications²⁰² can also lead to broadening the device configurations developed in this area.

s which can result in the conversion of $\text{CH}_3\text{NH}_3\text{I}$ into CH_3I and NH_3 ⁸. As

Fig. 12 (a) Solvent induced removal of Sn^{4+} where SnI_4 (i) forms a complex with DMSO (ii). The resulting $\text{SnI}_4 \cdot (\text{DMSO})$ interacts with non-polar toluene (iii). SnI_4 can also interact with other non-polar aromatic molecules such as benzene.²⁰³ Reproduced from Ref. 203 with permission from The Royal Society of Chemistry. (b) photograph showing the oxidation of Sn^{2+} to Sn^{4+} in air and the reduction of Sn^{4+} to Sn^{2+} in the presence of Sn powder.¹² Reproduced from Ref. 12 with permission from Springer Nature. (c) photograph of a highly specular MAPbI_3 spin coated based on the method reported by Noel et al.²⁰⁰ and the resulting (d) J - V characteristics of the champion device prepared by (i) annealing at 100°C for 1 hour (regular architecture), (ii) degassed under vacuum overnight and (iii) annealed at 100°C for 1 hour (inverted architecture). Reproduced from Ref. 200 with permission from The Royal Society of Chemistry.

Conflict of Interest

There are no conflicts of interest to declare.

Acknowledgements

K. D. G. I. J. and S. M. S. gratefully acknowledges financial support from the Equality Foundation of Hong Kong. R. K. M. gratefully acknowledge support and the European Commission H2020 CORNET program (Grant ID: 760949). S. M. S. Acknowledges support from the University of Surrey Vice Chancellors Scholarship Scheme. The authors also acknowledge the assistance provided by Dr Mozhgan Yavari at the Advanced Technology Institute, University of Surrey in preparing this review.

Notes

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