INTRODUCTION

Looking into the photovoltaic energy market by PV technology (Figure 1), it is evident the monopoly of the multi- and mono-crystalline silicon solar panels, owning a worldwide market share higher than 95%.1,2 This technology started being developed in 1954 as a power source for space equipments and has just begun being used for terrestrial energy applications at mid-1970s.3,4 Recently, the urge to fight climate changes and to reduce the carbon footprint has increased rapidly, mainly due to the change in the society’s mind set concerning sustainable development coupled with government incentive regulations. Consequently, the interest in building solar power plants and also the sales of domestic photovoltaic panels are expected to increase in the following years.

Currently, there is no other type of solar cell technology competing against silicon-based PV. However, like every technology, it has its own drawbacks. China is the world’s largest producer of silicon for solar panels, accounting for two-thirds of the global silicon-PV production.5 This centralization of solar industries makes it difficult for other countries to grow in this industry sector.5 After extraction, silicon dioxide undergoes a highly energy demand and...
expensive purification process at ~2000°C, usually powered by coal or other fossil fuel-burning plants. This means that silicon technology takes approximately 1.5 years to generate the equivalent amount of primary energy used to fabricate it.\(^6\) Besides, silicon processing releases a highly toxic substance—silicon tetrachloride.\(^7\) Finally, due to their rigid shape, size, colour limitations and opacity, silicon solar panels lack versatility regarding their final application. They may do well in solar farms, but bringing photovoltaics to our cities without compromising buildings’ aesthetics is a current struggle for architects and engineers.\(^8\) Moreover, the coronavirus pandemic outbreak was responsible for the cut on supply chains of semiconductor industries, which might be translated in a price increase of silicon-based technologies.\(^9\)

Regarding thin-film technologies, the ones being already commercialized include cadmium telluride (CdTe), copper indium gallium selenide (CIGS), gallium arsenide (GaAs) and amorphous thin-film silicon (a-Si). CdTe is the most common thin-film technology (Figure 1) because it is highly efficient (maximum lab PCE of 22.1%), cheaper than silicon devices and it is the thin-film technology with the lowest payback time and carbon footprint. However, cadmium is toxic and tellurium is scarce, turning large-scale production unsustainable. CIGS demonstrated to be a good alternative to CdTe since it does not use toxic metals and delivers high power conversion efficiencies (maximum lab PCE of 23.4%). Nevertheless, a scarce metal, indium, is still used and this technology is more expensive. Despite its earth abundance, non-toxicity and relatively low cost, a-Si has a low market share due to low power conversion efficiencies (maximum lab PCE of 14.0%). GaAs thin-film technology is the most efficient one (maximum lab PCE of 29.1%) but gallium is scarce and its manufacturing cost is very high, being used mainly for space applications.\(^10,11\)

There is still the category ‘emerging photovoltaics’ which are the not yet commercialized technologies (or commercialized with a very small market share). This category comprises dye-sensitized, perovskite, quantum dots, organic and inorganic solar cells. Regarding the perovskite solar cells (PSC), they are the emerging single junction photovoltaic with the highest efficiency (maximum lab PCE of 25.5%), closer to the crystalline silicon solar panels.\(^11\)

Furthermore, crystalline silicon solar panels have a thickness around 200 µm,\(^12\) whereas only ca. 400 nm (three orders of magnitude less) is required for the perovskite devices to equal silicon efficiency. In what concerns final usage, PSCs allow the possibility of different transparencies, colour-tuning and shape flexibility unlike silicon panels.\(^10\) Moreover, PSCs have already been used to power broadband photodetectors\(^13\) and synaptic devices (used in neuromorphic computing).\(^14,15\) In the later application, perovskite is able to mimic various synaptic functions because the migration of halide ions induced by light in the perovskite is similar to the redistribution of oxygen vacancies induced by external electrical pulses in the oxide-based memristors. This electrical induced migration process enables the control of the formation and breaking of conductive filaments, thereby mimicking synaptic functions.\(^15\) Apart from solar cells, perovskite materials have also a high potential as light-emitting diodes (LED) due to their adjustable band gap, high photoluminescence quantum yield and high colour purity.\(^16\) Based on the above-mentioned advantages of PSCs towards other photovoltaic technologies, the question is as follows: ‘Why PSCs are not yet commercialized?’ There are several critical features blocking their way to the commercialization as it is typical in emerging technologies. However, several research groups are now proposing very promising strategies to the cost, stability, upscaling and environmental impact challenges—Figure 2.

Concerning costs, one of the big advantages of perovskite technology is the variety of materials and processes that can be used to prepare a PSC device without compromising its efficiency. It is possible to fabricate a PSC using low-cost materials (such as carbon electrodes and inorganic selective layers) and with no high-consuming
energy steps as high processing temperatures or vacuum processes. For example, Ye et al. reported a PSC with 17.78% PCE using low-cost materials, no vacuum step and maximum temperature of 200°C. Then, stability is also a main topic of concern and Gracini et al. already reported a laboratorial-size PSC that operated one full year under 1 sun illumination and 55°C with no loss of efficiency. Towards upscaling goal and according to the National Renewable Energy Laboratory, the best performing perovskite module was fabricated in January 2020 by Panasonic and achieved a power conversion efficiency of 17.9% for a 802 cm² illuminated area. Finally, the use of lead is perhaps the major obstacle because of its high toxicity; however, removing it from the perovskite formulation without significantly compromising PCE has been proved to be an uphill battle. Nevertheless, the load of this metal in a perovskite solar module is low. Actually a square metre of a PSC panel contains only ~0.4 grams of lead (assuming 300 nm thick perovskite layer), which compared to other commercial lead containing devices is insignificant: one typical 14.5 kg lead-acid battery has 8.7 kg of lead. Additionally, solder ribbons used in some silicon solar panels contain 40% of lead. Additionally, strategies can be adopted to avoid lead leakage from the perovskite solar module in case of an accident, such as the coating of lead-absorbing materials or the use of a self-healing resin as sealant.

Besides the safety of the PSC devices, their recyclability is also of concern. Recent studies show that the perovskite layer at the PSC panels is easy to recycle and the substrates can be reused; this makes PSC panels more sustainable from the circular economy point of view.

Overall, several research groups have already overcome the major obstacles hindering perovskite device commercialization. According to Chinese reports, the first perovskite solar module (PSM) production line owned by the China-based company Microquanta Semiconductor, already started working on August 2020. However, no information was released concerning the features of this PSM. Microquanta also owns a 20 MW perovskite module pilot line. The USA-based Corporation Energy Materials has also a pilot scale-up manufacturing line working on PSM. Other companies working on the commercialization of this technology are the Hunt Perovskite Technologies (USA), Panasonic (Japan), Oxford PV (United Kingdom), Greatcell Energy (Australia), IMEC (Belgium) and Saule technologies (Poland). Detailed information about the PSC panel designs and manufacturing process from these companies is scarce. So, this review aims at to analyse thoroughly the most relevant and recent publications regarding the current PSC challenges in terms of costs, stability, upscaling and environmental impact. All the data are analysed holistically to identify the most suitable designs for reaching the market soon.

2 | POWER CONVERSION EFFICIENCY PROGRESS

Organic–inorganic perovskites were first studied by Weber in 1978 but only in 2006 this material was used as photovoltaic absorber by Miyasaka and co-workers. These authors were apparently attracted by the self-organization potential of perovskite on the nanoporous TiO₂ layer of dye-sensitized cells, reporting a PCE of 2.2% for devices prepared with methylammonium lead bromide (MAPbBr₃), lithium halide/halogen as redox couple and a Pt-coated FTO glass as counter-electrode. Three years later, replacing bromine by iodine from the perovskite, they were able to increase the PCE up to 3.8%. This PCE was further enhanced to 6.5% by Park et al. in 2011 using thinner nanoporous TiO₂ films and optimizing the perovskite coating solution concentration, post-annealing conditions and TiO₂ surface modification with Pb(NO₃)₂. One year later, the same authors demonstrated that the use of a solid hole conductor such as spiro-MeOTAD (2,2',7,7'-tetakis(N,N-di-p-methoxyphenyl) nylamine)-9,9'-spirobifluorene) makes the device stability to dramatically improve compared to MAPbI₃ with an electrolyte junction. This fact, together with the decrease in the photoelectrode thickness from 10 to 20 μm to below 1 μm, not only improved the stability but also boosted the reported PCE to 9.7%.

The period from mid-2012 until the end of 2013 was a very profitable period for perovskite research since important advances were made in the comprehension of perovskite-based devices and on reported PCE. First, it was reported the use of mixed-halide perovskites as MAPbI₃-xClₓ, which exhibited higher stability and enhanced carrier transport than its pure iodine analogue. Then, the nanoporous TiO₂ conductive scaffold was substituted by a non-conductive Al₂O₃ scaffold, coupled with the mentioned mixed iodine/bromine perovskite; these devices delivered more than 10.9% PCE under full solar illumination and an impressive open-circuit voltage of more than 1.1 V. This work demonstrated the wide potential of perovskite absorber to transport efficiently both holes and electrons. In mid-2013, Grätzel’s group used TiO₂ scaffolds and two-step iodine deposition for improving the perovskite morphology and reported a certified efficiency of 14.1%. Finally, as a consequence of the perovskite ambipolar transport ability, it was demonstrated that the TiO₂ scaffold was not essential to reach high energy conversion efficiencies and a simple planar device reached a solar-to-electrical efficiency of 15.4%.

In 2014, it was introduced the antisolvent crystallization method, where a solvent is poured onto the perovskite solution precursor during spin-coating, causing the
perovskite crystal to form and precipitate into a smooth and compact film. Seok et al.\textsuperscript{45} showed that when the perovskite was deposited using a mixture of γ-butyrolactone (GBL) and dimethyl sulphoxide (DMSO), followed by a toluene drip while spinning, extremely uniform and dense layers were formed. This solvent-engineering technology enabled a fully solution-processed PSC with a certified \textbf{16.2\%} PCE under standard reporting conditions. Another jump in the reported efficiency occurred by the hand of the same group, who further improved the PCE reporting a certified value of \textbf{17.9\%}.\textsuperscript{46} TiO\textsubscript{2} yttrium doping electron extraction layer was reported to improve the electron transport through the scaffold and modified ITO electrode work function, resulting in overall PCE of \textbf{19.3\%}.\textsuperscript{47}

In 2015, Seok et al.\textsuperscript{48} reported \textbf{20.1\%} of PCE with high-quality formamidinium lead iodide (FAPbI\textsubscript{3}) perovskite films without residual PbI\textsubscript{2}. A contact-passivation strategy, using chlorine-capped TiO\textsubscript{2} colloidal nanocrystal film, mitigates interfacial recombination and improves interface binding in low-temperature planar solar cells. Still using formamidinium with multiple cations and mixed-halide anions, Seok et al.\textsuperscript{49} showed that the introduction of additional iodine ions into the organic cation solution decreases the concentration of deep-level defects and is essential for realizing thin-film PSCs exceeding 21%; indeed, a certified power conversion efficiency of \textbf{22.1\%} was reached in June 2017.

In 2018, the PCE record was beaten twice by the same group—Chinese Academy of Sciences—first \textbf{23.3\%} and then \textbf{23.7\%}. Korea Research Institute of Chemical Technology together with the Massachusetts Institute of Technology did the same in 2019, achieving a PCE of \textbf{24.2\%} and then of \textbf{25.2\%}. In 2021, the Ulsan National Institute of Science and Technology in South Korea reached \textbf{25.5\%}, which is the current certified efficiency record. No further details about these devices were revealed by the respective groups. All these values were certified by the National Renewable Energy Laboratory.\textsuperscript{11}

This astonishing PCE progress throughout the years is summarized in Figure 3, together with the number of publications related to perovskite solar cells per year. Two main observations can be drawn: the number of publications is increasing every single year, and, in just 10 years, PCE has increased rapidly and now is reaching a plateau. Both conclusions are very promising and point out towards a bright future for perovskite solar technology. The increasing number of publications per year also indicates that the number of researchers interested in this technology is rising, which is also associated with higher budgets and projects approved in this field, and, this happens because investors and research support agencies believe on the PSCs potential.

3 | COSTS

To make the perovskite solar cells technology truly valuable for the society, a cost-effective approach must be adopted since only the fulfilment of a price target will give PSCs a chance to fly out of the research laboratories. Most researchers prefer PSC configurations based on expensive materials (e.g. spiro-OMeTAD and gold) and requiring highly energy-consuming processes (e.g. sintering at 500°C and thermal evaporation under high vacuum) since they display higher PCEs. However, perovskite devices are so versatile that several low-cost and moderately to high efficiency configurations are possible. Here we put together the information regarding the cost of most relevant materials, organized by their role in the device – Appendix S1. The objective of this study is to exclude the non-realistic materials for commercialization (too expensive, too rare) and narrow the path for defining the ultimate perovskite devices that can reach commercialization. For a complete cost analysis (that is not intended here), other information should be also considered such as PV system size and installation costs, module-level power electronics, operations and maintenance.\textsuperscript{50}

To allow a more correct comparison, all prices were collected from the same supplier—Sigma-Aldrich (unless said otherwise), the price considered was from high purity products and the biggest size available (taxes, shipping and handling not included). Prices were collected on June 2021. When materials are not commercially available, the authors of the articles reporting new synthesized materials were contacted to give a forecasted price. Obviously, this range of values are just for comparison and they are far from corresponding to the effective final prices of the raw materials at the commercialization phase. Additionally,
the cost of solvents is not presented because they vary according to the deposition method and also because they are much cheaper compared with the other raw materials. The thickness needed and the PCE achieved with each material are also presented. Thickness is an important parameter for a rough normalization of the effective layer cost, but they cannot be directly related because all these materials have different densities and porosities. It is also important to note that PCEs presented are from lab-size cells, and it will certainly decrease with device's active area. For that reason, and given the immensity of materials found, preference is given to the most efficient materials.

### 3.1 Substrate

Perovskite solar cells can be fabricated on flexible substrates, such as polyethylene terephthalate (PET) or polyethylene naphthalate (PEN). However, for this review, only rigid substrates are considered, given the lower performance and many processing restrictions associated with flexible substrates. There are two main glass substrates used for PSCs, which are indium tin oxide (ITO) and fluorine doped tin oxide (FTO)-coated glasses—Table 1. ITO has the advantage of being more conductive, transparent and smoother. However, it degrades under temperatures above 250°C and it is more expensive. Thus, the selection of the transparent conductive oxide (TCO) would depend on the trade-off between these features, considering the configuration processing constraints and performance goals. Additionally, the substrates may need patterning or scribing, which would account for additional expenses; Azzopardi et al. estimated that the TCO overall cost may account for about half of the total materials cost in an inverted PSC. Fortunately, these substrates can be easily reused without compromising their properties, which would be economically and environmentally advantageous in the long run.

### 3.2 Electron extraction layer

Traditional electron extraction layers (EEL) are mesoporous TiO$_2$ (for n-i-p architecture) and PCBM (for p-i-n architecture) with PCEs surpassing 23% and 20%, respectively. However, since mesoporous TiO$_2$ needs a sintering step at 450–500°C and PCBM is expensive (Appendix S1 – Table S2), both become economically problematic. Relevant EELs are presented in Table 2. Regarding n-i-p devices, there are other EELs that are as efficient and do not require very high-temperature annealing steps, which are as follows: planar TiO$_2$, NH$_2$-TiO$_2$ nanoparticles (NPs), SnO$_2$ (bare and with an extra layer of Al$_2$O$_3$ or ImAcHCl), TMAH, ZnO, WO$_3$ and 2D SnS$_2$. They all present PCEs higher than 19.9%, thickness lower than 60 nm, relatively low acquisition cost and maximum sintering temperature required of 150–180°C. Planar TiO$_2$ is particularly interesting given the high PCE (21.78%), low thickness (30 nm) and lenient sintering conditions (under air atmosphere at 150°C for 30 min). The most cost-effective EELs for p-i-n architecture are fewer: C60, NDI-ID and ITCTPC-Th. Even though C60 is deposited by a high energetic step (thermal evaporation under high vacuum), it is the only EEL raw material already commercialized among these three. Also, C60 can be combined by covalent bond with PDI, forming a material (PDI-C60) that can be deposited by spin coating. Important to mention that removing the electron extraction layer from the PSC design without significantly compromising the PCE is a hard task, since it is vital for the interfacial energy level alignment and, consequently, for effective electron extraction and transport with minimal charge recombination. Indeed, EEL-free devices are less common than devices without hole extraction layers (discussed next). Currently, the best EEL-free cell has a PCE of 19.5%.

### 3.3 Hole extraction layer

Numerous types of compounds can be used as hole extraction layer (HEL), such organic polymers, small molecules, metal-phthalocyanines, metal-porphyrines, chlorophylls and p-type inorganic semiconductors—Table 3 (complete list in Appendix S1—Table S3). Regarding the n-i-p architecture, the most used HEL is spiro-OMeTAD since it is the best performing one. However, it is also one of the most expensive. Others well-performing (PCE >20%) but not so expensive HELs are CuSCN, CuPc, PDO2, PHT-py, DBC-OMeDPA, OMe-TATPyr, DTP-C6Th and DTPC13-ThTPA. None of them need post-treatment, but only CuSCN and CuPc are already commercial. In what concerns p-i-n architecture, the expensive PTAA has proved to be the most efficient hole transporting layer. For the others, HELs are the annealing step rather than the acquisition price that increases the most the cost of the device. The pseudo-two-dimensional-conjugated Polysquaraine PASQ-IDT is the
**TABLE 2** Relevant EELs and information about the respective cell, for each architecture

| Architecture | Material             | Commercial | Used together with | PCE /% | Thickness / nm | Deposition conditions | Costa / (€/g) | Puritya /% | Materials for synthesis | Ref. |
|--------------|----------------------|------------|--------------------|--------|---------------|----------------------|--------------|----------|------------------------|------|
| n-i-p        | TiO₂ (planar)        | x          |                    | 21.78  | 30            | 150°C 30 min         | 0.24         | 98       | Titanium(IV) isopropoxide | 96   |
|              | NH₂-TiO₂ NPs (planar)|           |                    | 21.33  | 50            | 150°C 25 min         | 3.58         | NA       | NH₂-TiO₂ NPs             | 217  |
|              | SnO₂                 | x          |                    | 20.82  | 60            | 180°C 20 min         | 0.245        | 99.9     | SnO₂                    | 218  |
|              | Al₂O₃                |            |                    | 20.1   | 27            | 150°C 1 h            | 0.20         | 98       | SnCl₂·2H₂O               | 197  |
|              | doped with Nb 5%     |            |                    | 20.5   | 30            | Chemical bath deposition, 180°C 1 h | 0.20        | 98       | SnCl₂·2H₂O               | 220  |
|              | ImAcHCl              |            |                    | 21.43  | 9             | 150°C 25 min         | 0.245        | 99.9     | SnO₂                    | 221  |
|              | TMAH                 | x          |                    | 20.1   | 3             | 180°C 1 h            | 2.48 *€/mL   | NA       | TMAH                    | 222  |
|              | ZnO                  | x          |                    | 20.44  | 20            | 150°C 10 min         | 0.033        | 99.9     | ZnO                     | 223  |
|              | WO₃                  | x          | TiO₂ 7 nm          | 20.14  | 10            | 150°C 10 min         | 3.59         | 99.9     | WCl₆                    | 224  |
|              | 2D SnS₂              |            |                    | 20.12  | 2.4           | 180°C Langmuir–Blodgett deposition | 36.9        | 96       | SnS, similar compound    | 225  |
| p-i-n        | C60                  | x          | BCP                | 21     | 30            | Thermal evaporation under high vacuum | 134.2       | 99.5     | C60                     | 210  |
|              | NDI-ID               |            |                    | 20.2   | 40            | amb.                 | 125          | NA       | NDI-ID                  | 226  |
|              | ITCPCTC-Th           |            |                    | 17.1   | 5             | amb.                 | 270          | NA       | ITCPCTC-Th               | 227  |

*Relative to the material presented in the column ‘Materials for synthesis’.*
| Architecture  | Material Used together with | Commercial | PCE /% | Thickness /nm | Deposition conditions | Cost c / (€/g) | Purity c /% | Materials for synthesis | Ref. |
|---------------|-----------------------------|------------|--------|---------------|-----------------------|----------------|-------------|--------------------------|------|
| CuPc-b        |                             | x          | 20.09  | 40            | amb.                  | 143.5          | 99          | CuPc                     | 228  |
| PDO2-b        |                             |            | 20.2   | 110           | amb.                  | 55.148         |             | PDO2                     | 229  |
| PHPT-py-b     | Doped with Rutin–AgNPs      |            | 21.1   | 120           | amb.                  | 44.1           | NA          | PHPT-py, AgNO3           | 230  |
|               |                             |            |        |               | amb.                  | 2.78           | >99         |                          |      |
|               |                             |            |        |               | amb.                  | 1.396          | >94         | Rutin                     |      |
| DBC-OMeDPA    |                             |            | 22     | 150           | amb.                  | 13.217         | NA          | DBC-OMeDPA               | 231  |
| OMe-TATPyr     |                             |            | 20.6   | 115           | amb.                  | 45             |             | OMe-TATPyr               | 232  |
| DTP-C6Th      |                             |            | 21.04  | 40            | amb.                  | 18.16          |             | DTP-C6Th                 | 233  |
| DTPC13-ThTPA  |                             |            | 20.38  | 40            | amb.                  | 12.924         |             | DTPC13-ThTPA             | 234  |
| p-i-n         | P3CT-Rb                     | x          | 20.52  | 5             | 140°C 30 min          | 360            | NA          | poly[3-(4-carboxybutyl)thiophene] | 235  |
|               | NiO                         | Doped with Cs 1%mol | 19.35  | 23            | 275°C 1h              | 1.81           | >99.9       | caesium acetate | 236  |
|               |                             | Doped with Sr 1at% | 20.07  | 20            | 235°C 45min           | 1.52           | >99.5       | strontium chloride | 198  |
| PEDOT:PSS     | x                           |            | 20.6   | 25            | 150°C 30 min          | 6.56           | NA          | PEDOT:PSS                | 237  |
| DFH           |                             |            | 20.6   | 25            | 135°C 20 min          | 3.01           | NA          | DFH                      | 238  |
| TFB           |                             |            | 20.2   | 1.5           | 150°C 10min           | 723            | NA          | TFB                      | 239  |
| MPA-BTTI      |                             |            | 21.17  | 10            | 110°C 10min           | >480           | NA          | MPA-BTTI                 | 240  |
| 2PACz         | x                           |            | 20.9   | 130           | 110°C 10min           | 480            | >98         | 2PACz                    | 241  |
| MeO—2PACz     | x                           |            | 20.4   | 130           | 110°C 10min           | 460            | >98         | MeO—2PACz                | 241  |

*aSupplier.*  
*bNeed dopants.*  
'cRelative to the material presented in the column ‘Materials for synthesis’.
most promising HEL that does not require any sintering. Among the best HELs (PCE >19%), the ones with sintering steps at lower temperatures (<235°C) are P3CT-Rb, NiO (doped with Cs or Sr), PEDOT:PSS, DFH, TFB, MPA-BTI, MeO-2PACz and 2PACz. They are also very thin (thickness ≤25 nm), which makes their use more suitable and cheaper.

### 3.4 | Perovskite layer

The perovskite layer is the core of a PSC and its morphology and crystal quality is decisive for the device performance. Perovskite crystal consists in a ABX₃ crystallographic structure, where A is a large atomic or molecular cation (e.g. MA⁺, FA⁺, Cs⁺, Rb⁺), B is a small cation (Pb²⁺, Sn²⁺ or Ge²⁺), and X is a slightly smaller halogen anion (Br⁺, I⁺ or Cl⁺). Since there are plentiful precursors possible and more than one atom/molecule can be used with the same crystallographic function, there are an infinite number of arrangements possible for fabricating the perovskite layer. Regarding solvents, DMF, DMSO and NMP are the most used, but many others have already been reported with good performances. Among all PSC layers, this is the most challenging one, given the difficulty on flawlessly crystallize the perovskite precursor solution in large-scale substrates, and on make it environmentally safe and stable for long periods of time. Thus, the selection of the best perovskite crystal and fabrication conditions should depend more on the stability, upscaling and environmental impact rather than the cost. Anyway, the price of some precursors and solvents is also presented in Appendix S1—Table S8.

### 3.5 | Back-contact

The back-contact (BC) main function is to extract charge carriers from the device, so it must be highly conductive. The most conductive materials are undeniably metals, and indeed, numerous metals have already been tested as BC for PSCs. Besides conductivity, work function and chemical stability are another two crucial factors for a good BC. Gold is undoubtedly the best BC for n-i-p devices, with PCEs surpassing 22%, but it is also the most expensive metal. Beyond gold, only silver can be used for highly efficient n-i-p devices. Silver also works very well for p-i-n devices, as does copper, with PCE surpassing 21%—Table 4; between these two metals, copper is the cheapest one. There is still the possibility of using the same material of the front-contact as back-contact: metal oxides such as ITO and IZO. The big advantage is their transparency; however, part of the PCE is sacrificed due to conductivity restrictions.

Carbon-based materials may be the best alternative for a metal-free BC—Table 5. Their high chemical stability, conductivity, abundance, non-toxicity and ease for large-scale deposition make them very attractive for industrialization. In what concerns cost, the common carbon pastes made of graphite and carbon black are relatively cheap and only the more complex carbon materials, such as carbon nanotubes and graphene, may increase the final cost. In conventional n-i-p architecture, carbon is the last layer being deposited and so it cannot be subjected to high sintering temperatures for avoiding the degradation of the other inner layers. The best carbon-based conventional PSC consists in a self-adhesive carbon paste and resulted in PCE devices of up to 19.2%. Despite being cheap, carbon pastes do not require an annealing or other highly energy-consuming step. Another great advantage is the possibility of removing the HEL without significantly compromising the PCE. This simplification benefits the device stability, cost, fabrication process and environmental impact. For HEL-free devices, the present PCE record is 16.37% with an expensive back-contact of spray-coated SWCNT (10 nm). Similar PCE is achieved with a carbon paste as BC and with MWCNT as interfacial enhancer between the perovskite film and the BC—16.25%. Due to less extreme synthesis conditions, MWCNT are ca. 86 times cheaper than SWCNT, which makes the latter device more appealing. On the contrary, the use of carbon BCs in p-i-n devices is detrimental for the PCE because of the discordant energy levels of carbon materials and the lowest unoccupied molecular orbital (LUMO) of the typically used EELs. Only very recently (June 2020) a carbon paste was successfully employed in an inverted PSC. A 5-nm chromium layer between the EEL and the blade-coated carbon layer was added to solve the energy alignment issue. Using this strategy, Babu et al. achieved a very stable PSC with a

| Metal   | Architecture | PCE /% | Thickness / nm | Cost / (€·g⁻¹) | Purity/% | Ref. |
|---------|--------------|--------|----------------|----------------|---------|-----|
| Silver  | n-i-p        | 16.5   | 80             | 1.71           | 99.99   | 182 |
| Silver  | p-i-n        | 21.6   | 100            | 1.71           | 99.99   | 78  |
| Copper  |              | 22.5   | 80             | 0.316          | 99.99   | 210 |

TABLE 4 Reliable metals BC and information about the respective cell, for each architecture. Prices are from Kurt J. Lesker. Deposition method is thermal evaporation under high vacuum.
| Design            | Material       | Other modifications                          | PCE (%) | Thickness (nm) | Deposition conditions | Cost (€/g) | Purity (%) | Materials for synthesis | Ref. |
|------------------|----------------|----------------------------------------------|---------|---------------|-----------------------|------------|------------|------------------------|------|
| **Conventional** | Normal Carbon paste | TiO$_2$/SnO$_2$ double EEL                   | 17.78   | 40            | 80ºC 15 min           | 0.84       |            | Carbon paste            | 17   |
| HEL-free         |                | Carbon deposition modification                | 19.2    | 32,000 amb.   | 0.84                 |            |            | Carbon paste            | 59   |
|                  |                | MWCNT in perovskite/carbon interface         | 16.25   | $10^b$        | 140ºC 10 min$^b$      | 11.2       | >95        | MWCNT$^b$              | 242  |
|                  |                | TiO$_2$/PCBM double EEL                      | 14.37   | 70$^b$        | amb.$^b$              | 11.2       | >95        |                       | 243  |
|                  |                | TPA dopant in perovskite                     | 14.29   | 100ºC 20 min$^b$ | 0.07                 | 98         |            | TPA$^b$                | 244  |
| **Monolithic**   | Normal Carbon paste | Trication perovskite monolithic              | 17.02   | 10,000        | 80ºC 15 min           | 0.021      |            | Graphite               | 64   |
| HEL-free         |                | Ultrathin graphite                            | 14.07   | 2             | 400ºC 30 min          | 16.76      | NA         | Carbon black           | 245  |
|                  |                | Carbon paste CsBr as perovskite precursor    | 14.14   | 10,000        | 70ºC 10 min$^b$       | 2.06       | 99.9       | CsBr$^b$               | 246  |
|                  |                | Zn$^{2+}$ incorporated on perovskite          | 15.37   | 100ºC 10 min$^b$ | 6.88      | >99.99     | ZnI$_2$$^b$            | 66   |
|                  |                | 5-AVAI dopant on perovskite                  | 15.57   | 50 ºC 3.5 h$^b$ | 70.92     | >97        | $^a$TCI America$^a$    | 65   |

$^a$Supplier.

$^b$Relative to the materials presented in the column ‘other modifications’.

$^c$Relative to the material presented in the column ‘materials for synthesis’. 
| Layer function | Architecture | Material | Adjacent layers | PCE /% | Thickness / nm | Deposition conditions | Cost\(^a\) / (€/g) | Purity\(^a\)% | Materials for synthesis | Ref. |
|----------------|--------------|----------|----------------|--------|----------------|----------------------|----------------|----------------|----------------------|------|
| Passivating n-i-p | PMMA | Perovskite / DTP-C6Th (HEL) | 21.04 | 2 | 100°C 10 min | 0.36 | NA | PMMA | 233 |
| | Al\(_2\)O\(_3\) | FTO / Meso-TiO\(_2\) | 16.2 | 5 | ALD, 200°C | 4.19 | 97 | Trimethyl aluminium | 247 |
| | Cl-GO | Perovskite / PTAA | 21.08 | ? | ? | 132 | NA | Graphene oxide | 82 |
| | Reduced GO | CuSCN / Au | 20.2 | 10 | — | 543 | NA | Reduced GO | 80 |
| | LiF | C60 / Al | 18 | 1.2 | Thermal evaporation | 19.3 | 99.99 | LiF | 248 |
| | BCP | C60 / Cu | 22.5 | 3 | ALD, 200°C | 112 | 96 | BCP | 108 |
| | AZO | BCP / Ag | 18.45 | 40 | ALD, 200°C | 2.18 | >97 | Trimethyl aluminium diethyl zinc | 89 |
| | ZnO | PC61BM / Ag | 21.1 | ? | 100°C 10 min | 0.033 | 99.9 | ZnO | 249 |
| | TMPTA | Perovskite / PCBM | 20.26 | 10 | 140°C 20 min | 0.161 | NA | TMPTA | 83 |
| | Lead sulphate | Perovskite / C60 | 21.11 | 3.5 | — | 0.123 | 98 | Lead sulphate | 84 |
| Spacer (monolithic) n-i-p | ZrO\(_2\) | TiO\(_2\) / Carbon | 15.37 | 150 | 500°C 30 min | 0.1685 | 99 | ZrO\(_2\) | 66 |
| | Al\(_2\)O\(_3\) | TiO\(_2\) / NIO | 17.02 | 450 | 500°C 30 min | 0.186 | 99 | Aluminium acetylacetonate | 64 |

\(^a\)Relative to the material presented in the column ‘Materials for synthesis’.

TABLE 6 Relevant extra layers and information about the respective cell, for each architecture.
PCE of 15.18%. 60 Two other works can be found applying a carbon-based BC in this architecture, but with a much lower PCE and a more expensive carbon material (carbon nanotubes). 61,62 More recently, Ramachandran et al. reported an inverted PSC using a carbon back-contact with a record efficiency of 20.35% and a remarkable device stability and charge extraction. 63

Carbon materials can be used in monolithic structure. Though, high temperatures (ca. 500°C) are needed for this structure to anneal the EEL (e.g. TiO2), spacer layers (Al2O3 or ZrO2), HEL (e.g. NiO) and, frequently, also the carbon layer. Due to the uncontrolled and limited crystallization of the perovskite precursor solution, PCE obtained with the monolithic architecture is not as high as with the conventional one. Still, monolithic devices are easier to upscale because all their layers can easily be deposited by printing processes. A maximum PCE of 17.02% was achieved by a n-i-p monolithic device with a simple carbon paste (mixture of graphite, carbon black and zirconia) as BC. 64 For the HEL-free devices, the maximum PCE of 15.57% was reached with a carbon paste BC sintered at 400°C for 40 min and with an expensive perovskite dopant (5-AVAI). 65 Additionally, an impressive PCE of 15.37% was achieved with a carbon paste with a lower temperature annealing step (100°C for 20 min) and no dopants. 66

3.6 | Extra layers

There are other extra layers that can be used to increase either PCE (by improving the selective charge carrier’s extraction) or the stability—Table 6. For instance, the use of BCP between C60 and Cu improves device performance, but in the majority of the cases, their use is optional. Usually, these layers do not exceed 10 nm, and consequently, it will not have a significant influence on the final price of the device; unless, it is deposited by a highly energy-consuming process. Anyway, the more complex the system, the more fabrication issues can arise, and so the number of these extra layers must be minimized only to the absolutely essential.

3.7 | Final remark

From the cost point of view, it can be observed that some of the research most used materials are not industry-feasible, such as spiro-OMeTAD, PTAA, PCBM and gold. Though, most of them can be replaced by other cheaper materials that also attain reasonable PCEs, such as CuSCN-, NiO-, ZnO- and carbon-based BCs. There are other factors that will definitely affect the final cost device, like the deposition conditions (e.g. if an inert atmosphere is needed) and the deposition method itself (e.g. spin-coating wastes ca 90% of the material 67); these issues will be addressed further ahead. The most important thing to retain is that, given the immensity of materials that were already reported to prepare a PSC, and if commercialization is aimed, the raw materials must be firstly restricted just to the ones that are affordable for large-scale production. Nevertheless, it is likely that the final ideal device may need a more expensive layer to accomplish the other goals (stability, scalability and environmental impact).

4 | Stability

High efficiency of any photovoltaic technology is the primary target to convince the different stakeholders that is worthy to invest in a specific technology. This is what has been pulled forward in the last 5 years for perovskite solar cells. This strategy is quite obvious since a more efficient panel will produce more energy, and thus, it will have higher financial outcome. However, it is equally important the device stability because severe degradation pathways will be translated into a significant power loss with time and, in the limit, it may completely crash. 68 For an adequate stability assessment of new photovoltaic technologies, the International Electrotechnical Commission created the norm IEC 61215, which ‘lays down requirements for the design qualification and type approval of terrestrial photovoltaic modules suitable for long-term operation in general open air climates’. 69 Recently, the authors Holzhey and Saliba 70 focused on the analysis of the PSC answer to the different stability tests defined by this standard to assess its potential in entering to the commercialization stage. After analysing the stress tests suggested by the standard, they concluded that they designed based on previous knowledge of more mature photovoltaic technologies and they were not adequate to evaluate PSC degradation mechanisms. Thus, to properly determine the minimum stability requirements for a PSC to be commercialized, these stress test protocols have to be rethought and adjusted, as it was done previously for thin-film technologies such as CdTe and CIGS. In particular, light cycling and maximum power point tracking (MPPT) under continuous illumination for more than 100 h can be considered and other stress tests should be adapted, such as the hot-spot endurance, humidity freeze, damp heat, thermal cycling, hail and mechanical load stress tests. 70

Typically, a photovoltaic panel to be commercialized has to keep 80% of its initial PCE after 25 years of lifetime, that is a perovskite solar module starting with a PCE of 18%, after 25 years should still present a PCE higher than 14.4%. This challenging goal was overlooked for some time and only recently has been pursued by the PSC
research community, resulting in an exponential increase in the number of published works regarding this topic. It is then needed to adequately understand the degradation mechanisms of a PSC device to overcome the stability challenges. Degradation mechanisms can be divided into two categories according to the cause: intrinsic and extrinsic. An intrinsic degradation pathway is related to the cell operation: defects on the perovskite crystal structure, reactivity between adjacent layers, electrical field, temperature induced by light, whereas extrinsic is related to the environmental factors such as moisture, oxygen, heat and ultraviolet (UV) radiation.

Among all these degradation factors, moisture is the most severe because the perovskite has a polar nature and so when CH$_3$NH$_3$PbI$_3$ is exposed to moisture tends to hydrolyse to PbI$_2$, CH$_3$NH$_2$I and HI species. This reaction is visible through the change in colour from dark brown to yellowish. Another atmospheric hazard is oxygen since it diffuses into the perovskite layer and traps into the iodine vacancies, leading to the formation of PbI$_2$, CH$_3$NH$_2$, I$_2$ and water upon exposure to light. Thus, to ensure high efficiency, the perovskite fabrication must be performed in an inert atmosphere and the final device must be encapsulated in order to protect it from ambient humidity and oxygen. The usually employed perovskite is also thermally unstable and decomposes when exposed to temperatures higher than 85°C due to structural phase transitions. Apart from perovskite, there are many other selective layers sensitive to these environmental factors, in particular the hole transport materials. On the contrary, ultraviolet radiation is harmful to wide band gap EELs such as TiO$_2$ and Al$_2$O$_3$, which can be easily supressed by employing UV cut-off filters.

Several good solutions were already proposed to enhance PSC stability, such as the use of more stable charge extraction layers, synthesis of perovskite materials without non-reversible degradation pathways, fabrication of pure inorganic PSCs, mix of cations and halides in the perovskite layer configuration, use of additives, passivation materials and encapsulation. This section summarizes the most recent achievements regarding stable and efficient PSCs, so as to identify materials and strategies that fulfill the stability goal. As previously mentioned, there is no standardized holistic procedure for assessing PSC stability and so each laboratory has its own procedure. This discrepancy in the stability protocols makes it difficult to directly compare the results reported by different authors. Hence, to allow an accurate comparison between the stability data presented for the different PSC designs, it is only considered works with long-time MPPT (maximum power point tracking) data. MPPT is one of the soldest and most common tests performed by PSC researchers and consists in maintaining the PSC under constant 1-sun illumination and at a potential and current density that produces the highest power (i.e. maximum power point). In this way, it is possible to assess how a panel would behave if continuously working at full power. Moreover, the PCE is not inflated due to the hysteresis effect and its value corresponds to a stabilized and real value. However, due to the reversibility of some energy losses, periodic breaks in the stress test (mimicking a night rest) would result in a partial PCE recovering, and consequently in much more durable devices. This behaviour is related to ion and defect migration within the light-absorbing layer and to their accumulation at the light-absorbing layer interfaces.

Publications reporting MPPT data corresponding to more than 300 h were analysed and divided according to the stability enhancement strategy: adding, substituting or doping functional layers, perovskite crystal engineering and perovskite doping. The most promising results are summarized in Table 7. The maximum time tested was 2000 h. Akin et al. reported a n-i-p device with a thermally evaporated gold BC and with both extraction layers doped (Zn-TFSI$_2$-doped spiro-OMeTAD and Ru doped SnO$_2$) operating at MPPT for ~83 days—Figure 4A. An initial PCE of 22.0% was reached and only 3% of its initial PCE was lost after 2000 h at MPP, 25°C and under a nitrogen flow. However, the cell did not undergo a thermal stress test. On the contrary, Grätzel and his co-workers also reported a device tested through 2000 h at MPP but under 60°C, in a nitrogen atmosphere. The device had inorganic extraction layers (TiO$_2$ as EEL and CuSCN as HEL) and a graphitic carbon paste deposited at room temperature as BC—Figure 4B. The initial PCE was 18.1%, with a 5% PCE loss after the thermal stress test.

There are also other two highly efficient (PCE around 21.7%) and stable devices, tested at MPP during 800 h, but with no thermal stress test is reported. One was again described by Akin, but this time the strategy was to use caesium fluoride-doped SnO$_2$ as EEL and a zwitterion passivation layer between spiro-OMeTAD and gold. The n-i-p device retained 90% of its initial PCE. The other device was reported by Ning and his co-workers. Incorporating secondary amines in the perovskite layer, not only stability (device retained 80% of its initial PCE after the MPPT) but also PCE of the PSC increased, making these devices the most efficient inverted PSCs at the time of its publication. Other materials used for stability enhancement were tested, as tBBAI, PEAI, Zracc, 2PDI-4S, HMB, P-Si, Z26 and 5-AVAI, but they lack on thermal evaluation. Interestingly, only one work presented in Table 7 has a carbon-based BC. It was reported that metal BC can diffuse into the PSC inner layers if exposed to temperatures above 70°C, and so it was expected to find more
| Device structure                                                                 | Stability strategy                     | Active area / cm² | Initial PCE /% | Remained PCE /% | MPP conditions | Ref. |
|----------------------------------------------------------------------------------|----------------------------------------|-------------------|----------------|----------------|----------------|------|
| *Substitutional layers*                                                           |                                        |                   |                |                |                |      |
| FTO/c-TiO₂/meso-TiO₂/perovskite/CuFeO₂/Au                                       | CuFeO₂ as HEL                         | Lab               | 15.60          | 85             | amb            | 1000 | x   | 88  |
| FTO/c-TiO₂/meso-TiO₂/perovskite/CuSCN/Carbon                                      | CuSCN as HEL, carbon BC               | Lab               | 18.10          | 95             | 60             | 2000 | x   | 76  |
| FTO/NiO(ALD)/perovskite/PCBM/BCP/AZO(ALD)/Ag                                     | NiO as HEL                            | Lab               | 18.45          | 86.7           | 85             | 500  | x (with 50 nm Al₂O₃) | 89  |
| FTO/NiO/perovskite/PC₆AlBM/AZO/Ag                                                 | Sputter-deposited polycrystalline NiOx as HEL | Lab               | 15.2           | 73             | 85             | 1000 | ~5% RH | 90  |
| ITO/perovskite/C₆O₂/SnO₂/IZO                                                      | No HEL and IZO as BC                  | Lab               | 14.2           | 100            | amb            | 1000 | x   | 93  |
| FTO/Zn₂SnO₄/perovskite/spiro-OMeTAD/Au                                           | CBD-modified Zn₂SnO₄ as EEL           | Lab               | 21.3           | 90             | 25             | 1000 | x   | 87  |
| *Additional layers*                                                               |                                        |                   |                |                |                |      |      |
| ITO/SnO₂/perovskite/Cl-GO/PTAA/Au                                                | Chlorinated graphene oxide            | 1.02              | 21.08          | 90             | 60             | 1000 | x   | 82  |
| FTO/c-TiO₂/meso-TiO₂/perovskite/CuSCN/rGO/Au                                     | Reduced graphene oxide                | Lab               | 20.2           | 95             | 60             | 1000 | x   | 80  |
| ITO/P3CT-N/Perovskite/TMPTA/PCBM/C₆O₂/TPBi/Cu                                     | TMPTA                                  | Lab               | 20.26          | 80             | 60             | 1000 | ?   | 83  |
| ITO/PTAA/perovskite/lead sulphate/C₆O₂/BPC/Cu                                     | Lead sulphate                         | Lab               | 21.1           | 96.8           | 65             | 1200 | x   | 84  |
| FTO/TiO₂/perovskite/PPDT2FBT:BCF/PEDOT:PSS/ITO                                    | laminated device, PPDT2FBT:BCF as hole transporting glue layer | 1               | 17.3           | 86             | 85             | 1000 | 85% RH | 86  |
| FTO/NiOₓ/KCl/perovskite/KCl/PCBM/BPC/Ag                                           | Evaporate KCl at perovskite interfaces | Lab               | 19.2           | 90             | 45             | 1000 | x   | 85  |
| *Doping functional layers*                                                        |                                        |                   |                |                |                |      |      |
| FTO/TiO₂/perovskite/spiro-MeOTAD/Au                                              | Zn-TFSI2 dopant on spiro-OMeTAD       | Lab               | 21.11          | 100            | amb            | 600  | x   | 208 |
| *Perovskite crystallization engineering*                                          |                                        |                   |                |                |                |      |      |
| FTO/c-TiO₂/perovskite/Spiro-MeOTAD/Au                                            | Br-rich seeding growth method—(FA,MA, Cs)Pb(I, Br)₃ | Lab               | 21.50          | 80             | amb            | 500  | x   | 96  |
| FTO/c-TiO₂/meso-TiO₂/MAPbI₂/PTAA/Au                                              | MAPbI₂                                 | Lab               | 17.60          | 100            | 20             | 1000 | x   | 81  |
| FTO/c-TiO₂/meso-TiO₂/MAPbI₂/PTAA/Au                                              | MAPbI₂                                 | Lab               | 17.60          | 85             | 95             | 500  | x   | 81  |
| FTO/c-TiO₂/meso-TiO₂/perovskite/Spiro-MeOTAD/Au                                  | CsPbBr₃ cluster-assisted crystallization—(FA, Cs)Pb(I, Br)₃ | Lab               | 21.78          | 82             | amb            | 1000 | x   | 94  |
| FTO/c-TiO₂/meso-TiO₂/perovskite/Spiro-MeOTAD/Au                                  | CsPbI₂Br                               | Lab               | 14.46          | 86             | 85             | 1000 | ?   | 97  |
| FTO/c-TiO₂/meso-TiO₂/perovskite/spiro-MeOTAD/Au                                 | RbCsMAFA-based perovskite              | Lab               | 21.6           | 95             | 85             | 500  | x   | 98  |

(Continues)
| Device structure | Stability strategy | Active area / cm² | Initial PCE /% | Remained PCE /% | MPP conditions | Ref. |
|------------------|--------------------|------------------|----------------|----------------|----------------|-----|
| ITO/PTAA/perovskite/PCBM/ZnO/Al | Facile partial ion-exchange on perovskite | Lab | 16.8 | 93 | 60 1000 | x | 99 |
| ITO/PEDOT:PSS/2DRP perovskite/PCBM/Cr/Au | 2DRP perovskite | Lab | 18.06 | 85 | amb 1000 | x | 101 |
| FTO/c-TiO₂/meso-TiO₂/perovskite/SpriTO-MeTAD/Au | MDACl₂ in α-FAPbI₃ | Lab | 23.70 | 90 | amb 600 | x | 102 |
| FTO/c-TiO₂/meso-TiO₂/perovskite/SpriTO-MeTAD/Au | 1% ETI in MAPbI₃ | Lab | 19.51 | 83 | amb 600 | x | 103 |
| ITO/SnO₂/perovskite/spiro-O-MeTAD/Au | 0.1% NaF in CsMAFA | Lab | 21.46 | 90 | amb 1000 | x | 104 |
| ITO/SnO₂/perovskite/spiro-O-MeTAD(modified)/Au | Eu(acac)₃ in (FAMA, Cs)Pb(I, Br)₃(Cl) | Lab | 21.52 | 91 | amb 500 | ? | 105 |
| FTO/c-TiO₂/meso-TiO₂/perovskite: bis-PCBM/spiro-O-MeTAD/Au | α-bis-PCBM as antisolvent in MAFA | Lab | 20.8 | 96 | amb 600 | x | 106 |
| FTO/c-TiO₂/meso-TiO₂/perovskite: bis-PCBM/spiro-O-MeTAD/Au | bis-PCBM as antisolvent, BrPh-ThR in MAFA | Lab | 21.7 | 90 | 55 1500 | x | 107 |
| ITO/PTAA/perovskite/C60/BCP/Cu | Oleylamine in CsFAMA | Lab | 23.0 | 102 | amb 1000 | x | 108 |
| ITO/PTAA/perovskite/C60/BCP/Ag | 4-phenylpyridine in MAPbI₃ | Lab | 21.12 | 90 | amb 600 | x | 250 |
| ITO/P3CT-N/perovskite/PC61BM/C60/BCP/Ag | PbPyA in MAPbI₃ | Lab | 19.96 | 93 | amb 540 | x | 109 |
| ITO/P3CT-N/perovskite/PCBM/C60/BCP/Cu | TMPTA in MAPbI₃ | Lab | 20.22 | 80 | amb 400 | ? | 110 |

n-i-p structure; p-i-n structure (bold).
stability tests considering carbon BC. However, devices with metal BC present always higher efficiency due to high metal conductivity, better interfacial properties and possibility of back reflection of transmitted photons by the metal BC. Thus, authors opt for using blocking layers (e.g. chromium\(^{79}\) or rGO\(^{80}\)) or functional layers more resistant to metal diffusion (e.g. CuSCN\(^{80}\) or PTAA\(^{81}\) instead of spiro-OMeTAD), rather than sacrifice the device PCE. Nevertheless, bearing in mind an industrial product, this alternative is more expensive and may represent only a small increment in the final PCE. Basically, since both materials are scalable (metals are deposited by thermal evaporation under high vacuum and carbon is printed), the choice of the BC—metal or carbon-based—is a trade-off between cost and efficiency.

4.1 Functional layers

An important degradation pathway of PSCs is related to the active layers decomposition (HEL, EEL, back-contact and other extra layers), which is more noticeable for organic materials, such as spiro-OMeTAD or PEDOT:PSS, and interface interaction, where adjacent materials can migrate into each other or react with the surface constituents from the adjacent layers. A straightforward way to decrease these interfacial interactions is to add a passivation interlayer able of hindering migration and unwanted surface reactions without compromising the charge flow.\(^{71}\) For the n-i-p configuration, two graphene-based layers were proposed: chlorinated graphene oxide between the perovskite and HEL,\(^{82}\) and reduced graphene oxide between the HEL and gold BC.\(^{80}\) The chlorinated graphene oxide (Cl-GO) forms strong chemical bonds with the perovskite surface, resulting in the enhancement of the selective extraction of photogenerated charge carriers and the protection of the organic HEL from perovskite’s decomposed components.\(^{82}\) Grätzel’s group used reduced graphene oxide (rGO) for preventing non-desired reactions between gold BC and thiocyanate anions from the CuSCN HEL, induced by the electrical potential. Devices prepared following both strategies were tested during 1000 h at MPP and 60°C. Cl-GO-based devices kept 90% of its initial PCE (21.08%), whereas cells passivated with rGO kept 95% of its initial PCE (20.2%). Despite the high cost of these graphene-based materials, they are so thin (ca. 10 nm) that the stability improvement may compensate the higher price. Both passivation layers are truly effective (Table 7) and can be employed regardless the EEL, HEL and perovskite crystal selected. However, rGO will only be useful if the BC is a metal.

Concerning p-i-n inverted devices, a trimethylolpropane triacrylate (TMTPA) layer can be used to block ion migration between the perovskite and EEL either caused by heat, electric field or light, and it even improves initial PCE up to 8.7%.\(^{83}\) The PSC with this extra layer endured 1000 h at MPP and 60°C until losing 20% of its initial PCE. Given its low price and mild sintering conditions (140°C for 20 min), the net balance of using it is positive. Nevertheless, lead sulphate passivation layer is even more attractive because it is cheaper and thinner (3.5 nm), and devices with this layer are also more stable and efficient than with TMTPA layer—only a 3.2% PCE drop is observed after 1200 h at 65°C and MPP. Shortly, lead sulphate deposited above the perovskite layer boosts the PSC efficiency and stability by passivating the undercoordinated surface lead centres that act as defect-nucleating sites.\(^{84}\) Alternatively, Zhang et al. passivated both perovskite interfaces with a thermal evaporated potassium chloride (KCl) thin film (20 nm and 3 nm at the perovskite interface with HEL and EEL, respectively). In addition to passivating the perovskite surface defects and accelerating the charge extraction, the KCl layer between the HEL and the perovskite also contributes for an increased perovskite crystallinity. The incorporation of both KCl passivation layers results not only in a very stable PSC (retained 90% of its initial PCE after 1000 h at MPPT), but also increased PCE by 12% (from 17.1% to 19.2%).\(^{85}\) Finally, a different strategy to build a PSC is to sequentially deposit the layers in two separate substrates—FTO/EEL/perovskite and...
I T O / H E L — and join the two parts with an electrical glue-like PPDT2FBT:BCF. However, the electrical glue layer is thick (500 nm) and costly (1260 €/g), which would make the final device too expensive.86

Instead of adding layers that may contribute to fabrication complexity, some authors replaced the typical used functional layers by others more stable, usually inorganic. Sadegh et al. demonstrated that employing Zn2SnO4 as EEL in a planar device, instead of TiO2, resulted in a very stable PSC: a PSC loss of 10% of its initial PCE (21.3%) after 1000 h at MPPT. The Zn2SnO4 layer was deposited by a sol–gel-derived spin-coating approach and underwent a chemical bath deposition for surface treatment.87

Regarding the HEL, unlike typical HELs (spiro-OMeTAD and PTAA), none of the alternative layers presented in Table 7 are costly unbearable: CuFeO2,85 and CuSCN for n-i-p devices and NiO for p-i-n. By Table 7, it can be observed that CuFeO2 is not so efficient nor stable than the device with CuSCN HEL reported by Grätzel76 (already mentioned before). Interestingly, Grätzel’s group presented two PSCs with similar designs, only differing in the BC. Not surprisingly, the cell with rGO/Au BC80 is more efficient but the cell with carbon BC76 is more stable: rGO/Au cell has a PCE of 20.2% and degraded 95% after 1000 h at MPPT; carbon BC cell has a PCE of 18.1% and degrade 95% after 2000 h at MPPT. For the inverted structure, NiO was the only material tested to replace the organic PTAA and PEDOT:PSS typical HELs—Figure 5.89,90 In addition to its higher stability, NiO can be deposited by several scalable processes such ALD,91 electrochemical deposition92 and spray pyrolysis.92 In the last work referenced in Table 7 regarding substitutional layers, it can be found the strategy proposed by McGehee’s group considering the replacement of the typically used metal BC by sputtered indium zinc oxide electrode (200 nm) in a HEL-free device. The thermal and environmental stability was indeed very good (no PCE loss during 1000 h near MPP and 85°C) but the initial PCE achieved was not that high (14.2% for a lab cell).93

As an alternative, instead of replacing spiro-OMeTAD, Grätzel’s team doped it with Zn-TFSI2 salt. When compared to the spiro-OMeTAD film doped with the typical Li-TFSI salt, this new dopant allowed a higher hole mobility (by one order the magnitude) and a higher recombination resistance, which was translated in a PCE increase by 10%. Also, due to the inhibition of lithium cation migration induced by Li-TFSI dopant, PSCs based on spiro-OMeTAD with Zn-TFSI2 presented no loss in the PCE during 600 h at MPPT, whereas PSCs based on Li-TFSI dopant lost ca 15% of its initial PCE. Although spiro-OMeTAD stability was enhanced, its high cost is still a major concern, blocking its usage in commercial perovskite solar modules.

4.2 | Perovskite layer

There are several effective strategies to hinder the degradation rate of the perovskite material. In almost all these strategies, the perovskite film is deposited by spin-coating since it is the method that minimize the perovskite defect density. Though, this method is unlikely to be scaled up, which is a major limitation towards commercialization. Besides, perovskite crystallization is highly dependent on the deposition technique and so spin-coating optimization strategies may not be applied to other deposition processes. Still, it is fruitful to understand the perovskite crystallization mechanisms, as well as the behaviour and interactions of some dopants with the perovskite crystals.

4.2.1 | Crystallization engineering

Perovskite crystallization can be stabilized through the interplay of the crystal cations and anions within the Goldschmidt tolerance factor for the cubic perovskite structure and preserving a proper bandgap (predicted optimal bandgap is 1.34 eV).94 On Table 7 are listed promising perovskite crystal stabilization techniques. It can be observed that iodine is the most used anion, allowing a suitable bandgap (1.3–1.4 eV) when used coupled with a small concentration of bromide anions ((FAPbI3)x−(MAPbBr3)y, where x is less than 0.05). Wider bandgaps are reached with higher bromide concentrations compromising the PCE but enabling better long-term operational and thermal stability: iodine anions migrate easily under operation (due to their lower ionic migration activation energy) and bromide anions thermodynamically favour the FAPbI3 black phase.95 Li et al.96 obtained a stable 21.5% PSC through a Br-rich seeding growth method—Figure 6. Fluoride is also an effective stabilizer since it passivates...
vacancies on the surface and grain boundaries, as already mentioned before. Chlorine retards the perovskite crystallization by reducing the number of nucleation sites, which leads to a better performance (due to the larger grains), but have no influence on the stability.96

Regarding the big cation, practically all highest performing PSCs use methylammonium (MA), even if in small amounts. However, MAPbI₃ perovskite when exposed to high temperatures can degrade into CH₃NH₂, HI and PbI₂, or degas as CH₃I, NH₃ and PbI₂. MA cations can also penetrate into some organic HELs such spiro-OMeTAD creating deep-level trap states.81 Even so, Saliba and his co-workers reported an impressive MAPbI₃-PSC that lost no efficiency during 1000 h at MPPT, and just lost 15% of its initial PCE after 500 h at 95°C under constant illumination. Nevertheless, under open-circuit voltage, the devices degrade significantly (~70% PCE loss in 250 h at 65°C under constant illumination).81

Formamidinium (FA) has a better thermal stability than MA due to stronger hydrogen bonding interactions within the perovskite. However, the desired α-phase of the FA-based perovskite spontaneously transits to the δ-phase when exposed to ambient moisture. Incorporating together smaller A-site cations, such as Caesium (Cs) and MA, tune the Goldschmidt tolerance factor, inhibiting that spontaneous transition. For instance, Xie et al. fabricated an α-phase pure FAPbI₃-based PSC (Cs:FA = 0.05:0.95) with a PCE of 21.78% by CsPbBr₃-cluster assisted vertically bottom-up crystallization—Figure 7.94 The device kept 82% of its initial PCE after 1000 h at MPP. CsMAFA-based perovskites are also more reproducible and thermally stable than MA/FA mixture. This triple cation perovskite recipe has proven to be very interesting in terms of both performance and stability, being for that reason defined as the standard perovskite recipe. Indeed, the article written by Grätzel’s group in 2016 proposing this new recipe has over 2600 citations.95 Using just Cs as the big cation instead of just adding a little percentage, such the all inorganic CsPbI₃Br-based PSC reported by Kim et al., demonstrated great stability too: after 1000 h at 85°C and MPP the device lost 14% of its initial PCE. However, its wide bandgap (~1.92 eV) makes the initial PCE fall to 14.46%.97 It can still be embed a fourth cation—rubidium (Rb)—to further stabilize the black phase of the FA perovskite: the more the inorganic cation concentration in the perovskite, the more the entropy of mixing, resulting in a crystal stabilization. Although Rb is not suitable for a pure RbPbI₃ compound (contrary to Cs, MA and FA), a 5% Rb addition resulted in a stability enhancement (5% PCE loss after 500 h at 85°C and MPP), maintaining a high PCE of 21.6% even with a bandgap of ~1.63 eV.98

Fu et al.99 designed an original strategy—compositionally grade the perovskite absorber layer—in order to create an additional electrical force (induced by the grading bandgap) that promotes the drift of photogenerated charge carriers to the respective contacts—Figure 8. Thus, interfacial radiative recombination is suppressed, and the charge collection is enhanced. This was accomplished by partial ion-exchange. Briefly, MAPbI₃ was firstly deposited by a hybrid thermal evaporation/spin-coating method, then MABr was spin-coated to induce a halide ion-exchange, and, finally, the perovskite film was thermally annealed under chlorobenzene vapour atmosphere to promote ions diffusion and redistribution.
and crystal growth. Comparing with the usual MAPbI$_3$ perovskite, this gradient bromide incorporation boosted the operational stability: 7% PCE drop after 1000 h at 60°C and MPP. However, given the low-scale and complex fabrication process, the partial ion exchange has to be simplified and adapted to large-scale deposition to become commercially viable.

All the aforementioned perovskite structures are three-dimensional, but it is also possible to fabricate two-dimensional (2D) perovskites that consist in aligned perovskite layers with a long-chain occupying the (total or not) A sites of the crystal. The 2D perovskite, besides differing in numerous optoelectronic properties, they have enhanced stability in ambient environment. One particular kind, known as 2D Ruddlesden-Popper (2DRP) perovskite, presents good stability because it naturally has quantum well structures that exhibit quantum confinement effects without physically thinning down to the atomic thickness. The device fabricated by Ren et al. lost 15% of its initial PCE (certified 17.8%) after 1000 h at MPP, demonstrated moisture tolerance during 1512 h under 70% relative humidity (RH) and thermal stability for 375 h at 85°C. The fabrication method used was the two-step spin-coating, which is more reproducible and likely scalable than the antisolvent method used in the previous two studies. Contrary to MDA and ETI, NaF is incredibly cheap, and the MPPT period was also wider. Moreover, NaF-doped PSC withstands 1000 h at 85°C losing only 10% of its initial PCE and loses also only 10% of its initial PCE after 6000 h under a relative humidity of about 25–45% and temperature between 25°C and 40°C.

Another additive used for passivating vacancy defects in the perovskite bulk, which hinder their dissociation and migration, and also blocks the material degradation pathways at the perovskite interfaces. The deposition method used was the two-step spin-coating, which is more reproducible and likely scalable than the antisolvent method used in the previous two studies. Contrary to MDA and ETI, NaF is incredibly cheap, and the MPPT period was also wider. Moreover, NaF-doped PSC withstands 1000 h at 85°C losing only 10% of its initial PCE and loses also only 10% of its initial PCE after 6000 h under a relative humidity of about 25–45% and temperature between 25°C and 40°C.

4.2.2 Doping

New compounds can also be added to the perovskite precursor solution to stabilize the favourable crystal. The first dopant listed in Table 7 is methylenediammonium dichloride ($\text{MDACl}_2$). It is known that FaPbI$_3$ is more thermally stable than MaPbI$_3$; however, the desired FaPbI$_3$ trigonal black $\alpha$-phase decomposes easily under ambient conditions to the undesired wide-bandgap $\delta$-phase with hexagonal symmetry. Since methylenediammonium (MDA) has more hydrogen atoms than formamidinium (FA) and methylammonium (MA), it can form a greater number of H bonds with I, maintaining and stabilizing the inherent bandgap of FAPbI$_3$ $\alpha$-phase in smaller amounts that MA does. Consequently, by doping perovskite with MDACl$_2$, Seok’s team improved the PSC stability (cell lost 10% of its initial PCE after 600 h at MPP) and PCE up to a certified value of 23.7%. MDACl$_2$ is more expensive than the typically used perovskite precursors; however, the amount needed is so small ($\text{Fa}_{0.963}\text{MDA}_{0.037}\text{PbI}_3\text{(C}_\text{li})_{0.037}$) that the stability improvement may compensate this overcharge (PCE only increases 2% comparing to FAPbI$_3$).

An effective dopant for the MAPbI$_3$ perovskite is the ionic liquid 1-(4-ethenylbenzyl)-3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoroctylimidazolium iodide (ETI). Adding 1% of ETI retards the MAPbI$_3$ perovskite decomposition by impeding the migration of degraded MA, which results in an effect similar to MDA: little increase in PCE (1.6%), but significant stability enhancement. PSC doped with ETI also demonstrated good stability under a relative humidity of 35−45%, losing only 20% of its initial efficiency after 700 h at MPP. However, comparing to MDA, ETI is costlier and less efficient (PCE of 19.51%).

Next, a certified PCE of 21.3% was achieved in a planar device with 0.1% sodium fluoride ($\text{NaF}$) in the CsMAFA perovskite ($\text{(Cs}_{0.05}\text{FA}_{0.54}\text{MA}_{0.41})\text{Pb}(\text{I}_{0.98}\text{Br}_{0.02})_3$). The fluoride inorganic salt passivates both cation and anion vacancy defects in the perovskite bulk, which hinder their dissociation and migration, and also blocks the material degradation pathways at the perovskite interfaces. The deposition method used was the two-step spin-coating, which is more reproducible and likely scalable than the antisolvent method used in the previous two studies. Contrary to MDA and ETI, NaF is incredibly cheap, and the MPPT period was also wider. Moreover, NaF-doped PSC withstands 1000 h at 85°C losing only 10% of its initial PCE and loses also only 10% of its initial PCE after 6000 h under a relative humidity of about 25−45% and temperature between 25°C and 40°C.

Another additive used for passivating vacancy defects is europium(III) acetylacetonate hydrate ($\text{Eu(acac)}_3$). A (FA, MA, Cs)Pb(I, Br)-based perovskite was also deposited by the typical two-step method, this time in a mesoporous EEL substrate. With 1% of Eu(acac)$_3$, the perovskite, PCE is also high (21.52%) and thermal stability is similar to the previous work, but MPPT is half the time and the additive is more expensive. Gratzel's team...
thought in a different strategy to incorporate the dopant (α-bis-PCBM) inside the perovskite—dissolve it in the antisolvent—Figure 9. Through this strategy, the α-bis-PCBM molecules filled the perovskite vacancies and grain boundaries, resulting in a PCE, stability and reproducibility improvement: PCE dropped 4% from its initial value of 20.8% after 600 h working at MPP and dropped also less than 10% during 45 days either in 40–60% RH at ambient temperature (encapsulated device) or at 65°C (encapsulated). In the following year, a similar approach was published by the same authors. Basically, since bis-PCBM acts as a Lewis acid, the advancement consisted in using N-(4-bromophenyl)thiourea (BrPh-ThR) as the Lewis base in the perovskite solution precursor in order to passivate both Pb²⁺ and PbX₃⁻ antisite defects. With this optimization, PCE rose up to 21.7% and stability at high temperature, moisture and under MPP also improved. However, bis-PCBM is tremendously expensive (3400 €/g) and the deposition method is not scalable.

Moving now to the inverted PSCs configuration, four works must be highlighted. To note that all of them have C60 as EEL and BCP as passivation layer, leading us to deduce that these are the most stable EEL and passivation layer for inverted PSC. Luckily, both are also scalable, very thin and reasonably affordable. Bakr’s work is certainly the most promising: a certified PCE of 22.3% for an inverted device without PCBM that endured 1000 h at MPP with no loss of PCE. The long chains of oleylamine (OAm), an alkylamine ligand, promote a favourable perovskite grain orientation; therefore, perovskite crystals with just 0.1% of OAm have a lower trap-state density, enhanced carrier mobilities and longer diffusion lengths. Consequently, the nonradiative carrier recombination in perovskite is suppressed and the optoelectronic properties are improved. Additionally, the OAm-doped device keeps ~90% of its initial PCE after 1020 h at 85°C, under a nitrogen atmosphere. Xu et al. used practically the same PSC design, only differing in the back-contact—Ag instead of Cu—and in the ligand used as perovskite dopant—4-phenylpyridine (4-pPy). The effect of 4-pPy is similar to that of OAm: it regulates the perovskite nucleation kinetics and stabilizes the crystal lattice. By doping the perovskite with 5 mg/mL of 4-pPy, a PSC endured 600 h at MPPT losing just 10% of its initial PCE (21.12%), which makes the ligand OAm a better dopant.

Two other dopants were proposed by Junfeng Fang, and they are used practically in the same device configuration (only metal BC is different). These dopants are used aiming to strongly interact with the perovskite grain boundaries and passivate its defects. This way, PCE is enhanced and the ion migration and component volatilization caused by environmental stresses are hindered. First, the synthesized hydrophobic pyridine-2-carboxylic lead salt (PbPyA₂) shows better operational stability (7% PCE loss after 540 h at MPP) but lower PCE (19.96%)—Figure 10. The cross-linkable trimethylolpropane triacrylate (TMPTA) lost 20% of its initial PCE (20.22%) after 400 h at MPP. Regarding the thermal stress test, these two compounds are similar: PbPyA₂ (TMPTA) lost 20% (18%)
of the initial PCE after ~480 h under 90°C (85°C) in a nitrogen atmosphere.

Considering the aforementioned information regarding perovskite dopants, it can be observed that dopants used by the different authors enhance the perovskite film stability by different mechanisms. Also, the morphology of substrate where the perovskite is being deposited (compact or mesoporous) and the perovskite crystal structure are decisive parameters for determining which dopant would work better. For instance, MADCl₂ is proper for a-FAPbI₃ perovskite and mesoporous substrate (TiO₂), while for a compact substrate (SnO₂) and CsMAFA perovskite, NaF is preferred. All in all, the dopant must be chosen according to the properties and flaws to mend of the crystal that is being produced, so as the final light-absorbing layer is fully optimized. Indeed, from previous overview, it can be identified very promising dopants for various perovskite configurations: MDACl₂ for FAPbI₃, ETI and PbPyA2 for MAPbI₃, NaF and OAm for CsMAFA and Eu(acac)₃ for (FA,MA, Cs)Pb(I, Br)₃.

**TABLE 8** List of the ten most promising encapsulation methods along with relevant data about the design of the encapsulated devices as well as thermal, moisture and MPP test results

| Device structure                          | Encapsulation material | Encapsulation method                                      | Thickness | PCE lost during encaps. /% | MPP Remained PCE% | RH / % |
|------------------------------------------|------------------------|----------------------------------------------------------|-----------|-----------------------------|-------------------|-------|
| FTO/c-TiO₂/ meso-TiO₂/ perovskite/ CuSCN/rGO/Au | PMMA                   | Spin-coating solution 20mg/mL in chlorobenzene atop the gold | 30 nm     | 0                           | —                 | —     |
| FTO/TiO₂/ perovskite/ spiro-OMeTAD/Au   | Parylene-C             | Vapour deposition technique, 1 Pa                         | 700 nm    | 0                           | —                 | —     |
| FTO/c-TiO₂/ meso-TiO₂/ perovskite/ spiro-OMeTAD/ Ag | Polyimide Tape        | Lamination                                               | 70 μm     | 0                           | —                 | —     |
| FTO/TiO₂/ZrO₂/ perovskite/ carbon (monolithic) | Polyurethane          | Lamination at 70°C, place glass above                      | ?         | 0                           | —                 | —     |
| FTO/NO(ALD)/ perovskite/ PCBM/BCP/ AZO(ALD)/Ag | Al₂O₃                  | ALD, 100°C                                              | 50 nm     | 0                           | 86.7 amb          |       |
| FTO/c-TiO₂/ meso-TiO2/perovskite /PTAA/Au | ALD, 95°C              | 50 nm                                                   | 12        | —                           | —                 | —     |
| ITO/SnO₂/ perovskite/ spiro-OMeTAD/Ag   | Alucone + Al₂O₃        | Molecular layer deposition, 80°C                          | 5.6 nm    | 0                           | —                 | —     |
| ITO/SnO₂/ perovskite/ spiro-OMeTAD/Au   | UVCA + paraffin        | Immerse glass in melted paraffin at 90°C, quickly place it above Au, let it dry, coat UVCA around, UV light | ?         | 0                           | 85 amb            |       |
| FTO/c-TiO₂/meso-TiO₂/perovskite/ Au     | UV-curable epoxy edge sealant | Dispensing epoxy resin around, place glass above, UV light | ?         | 15                          | —                 | —     |
| FTO/TiO₂/ZrO₂/ perovskite/ carbon (monolithic) | Glass frit            | Laser-assisted glass-frit encapsulation                   | 0         | —                           | —                 | —     |
A very important step of the perovskite fabrication is its final encapsulation, not only to protect the device from outdoor environmental degradation sources for reaching the desired lifetime, but also to avoid inner-components leakage. Materials typically used in silicon solar panels encapsulation are polyolefin and ethylene vinyl acetate but they are not proper for PSCs because they require high sealing temperatures that would degrade the perovskite. Thus, other strategies were already proposed to seal a perovskite device without damaging it, like lamination of a low-temperature melting polymer, edge-sealing and recourse to an insulating ceramic material instead of a polymer. Relevant encapsulation strategies were put together in Appendix S2—Table S12, and from this list, it was selected the top 10 most promising sealing processes based on the respective stability test outputs and encapsulation process complexity—Table 8.

It is important to underline that stability results are also dependent on the device configuration and materials, and so a linear comparison between encapsulation methods

| Thermal test | Moisture test |
|--------------|---------------|
| Remained PCE % | RH / % | T /°C | Time / h | Remained PCE % | RH / % | T /°C | Time / h | Ref. |
| 85 | 40–60 | 85 | 1000 | 100 | amb | amb | 196 | 111 |
| 86.1 | 30–70 | 85 | 1000 | 96.3 | Immersed in water | amb | 3min | 112 |
| 97 | amb | amb | 2136 | 113 |
| 99.5 | 20–60 | amb | 500 | 89 |
| 96 | 50 | amb | 7500 | 114 |
| 95 | Immersed in water | amb | 5 | 115 |
| 96 | 80 | 30 | 2100 | 117 |
| 83 | 50 | 30 | 1680 | 116 |
| 100 | 75–85 | amb | 500 | 118 |

### 4.3 Encapsulation

A very important step of the perovskite fabrication is its final encapsulation, not only to protect the device from outdoor environmental degradation sources for reaching the desired lifetime, but also to avoid inner-components leakage. Materials typically used in silicon solar panels encapsulation are polyolefin and ethylene vinyl acetate but they are not proper for PSCs because they require high sealing temperatures that would degrade the perovskite. Thus, other strategies were already proposed to seal a perovskite device without damaging it, like lamination of a low-temperature melting polymer, edge-sealing and recourse to an insulating ceramic material instead of a polymer. Relevant encapsulation strategies were put together in Appendix S2—Table S12, and from this list, it was selected the top 10 most promising sealing processes based on the respective stability test outputs and encapsulation process complexity—Table 8.

It is important to underline that stability results are also dependent on the device configuration and materials, and so a linear comparison between encapsulation methods...
is not possible. For instance, in the PSC with PMMA as encapsulation material, the true degradation inhibitor is in fact the rGO layer, because without it the PSC does not last more than 50 h at MPP without losing half of its initial PCE. Furthermore, this encapsulation material is deposited via spin coating, which is not scalable.80 Relatively to the parylene-C encapsulation method, parylene for coating is fabricated through 3 consecutive steps—vaporization at 170°C, pyrolysis at 690°C and polymerization at 20°C—and then it is deposited by vapour deposition at 1 Pa. Both parylene-C fabrication and deposition are highly energetic consuming, which for large-scale production is undesirable. Moreover, the parylene-C device was not tested under high temperature nor humidity.111 On the contrary, a simple and easy encapsulation method consists of just placing a heat resistant and waterproof polyimide tape (also known as Kapton®) above the device. Incredible, the device kept 86% of its initial PCE after 1000 h at 85°C and 30–70% RH, it even stood 3 min under water losing just 4% of its PCE and after 3 h at 240°C had a PCE drop of 9%.112 The major drawback is the relative high price of the Kapton® tape (341 €/m²) in comparison with other polymers such PET. Another even more expensive polymer used for encapsulation is polyurethane (2680 €/m²)— Figure 11. With this foam laminated at 80°C, the monolithic device endured 2136 h at ambient conditions with an insignificant drop of 3%, and no PCE loss was observed after 350 h at 85°C.113 The later stability result is indeed very appealing, but it has to be noted that the device configuration was monolithic, naturally more stable than using unstable selective layers such as spiro-OMeTAD or metal BC.

Apart from polymers, a ceramic isolating material was also reported as thin film sealant—alumina. Despite being typically used as passivation layer in PSCs, three of the listed works in Appendix S2—Table S11 present alumina deposited by atomic layer deposition (ALD) as encapsulation material. The conventional device fabricated by Park’s group endured the enormous period of 7500 h (> 10 months) at 85% RH, losing less than 4% of its initial PCE. Relatively to temperature stability, the device kept 87% of its initial PCE after 500 h under 85°C, MPP and ambient humidity.114 These are indeed very promising stability results for such a thin sealing layer (50 nm), but it should be pointed out that the PSC lost 12% of its initial PCE during alumina deposition at 95°C. Seo et al. opted for an inverted device, which endured 500 h exposed to 20–60% RH with less than 1% drop in PCE, and the same time at 85°C with a 13% PCE lost.89 Yang et al. introduced an ALD variation (plasma enhanced) that resulted in an increased moisture stability: the PSC withstood 2100 h
under 85% RH, loosing just 4% of its initial PCE. To protect the device active layers from plasma, an interlayer of alucone (5.6 nm) had to be added (by molecular layer deposition)—Figure 12.115

All the previous encapsulation methods consist of the deposition of a thin sealing film above the device active layers. Another strategy to seal a device is to deposit an encapsulation material around the device and seal it afterwards to a cover substrate. Through this method, less sealing material is spent and the probability of damaging the active layers is lower. Ramasamy et al. followed this approach and used a UV light curable epoxy resin as an edge sealant. The device suffered a 17% PCE loss after 1680 h at 30°C, MPP and under 50% RH, but 15% of the initial PCE was lost due to encapsulation. Moreover, the device was not tested under high humidity or temperature, and so it is not possible to perceive the sealant permeability to water or temperature resistance.116 Chen and his co-workers used the same strategy, but identified a problem: the atmosphere during sealing stays inside the device and boosts its degradation. Their solution was to fill the empty space inside the device with a low-cost, solvent-free and low-temperature melting polymer—paraffin (Figure 13). By merging the two encapsulation methods (thin film and edge sealing), a planar device retained 98% of its initial PCE after 2120 h at 50% RH and ambient temperature. The device was also tested under 65°C and 40–60% RH, and after 1000 h, it still had 90% of its initial PCE.117

Finally, the last work also consists in an edge-sealing method but demonstrated no need for an additional thin-film protective layer or an inert atmosphere during sealing. Briefly, a glass frit was deposited by screen printing method on both glass substrates (solar cell and cover glass); for low-temperature laser-assisted glass-frit sealing, the device is kept at 100°C and a laser is emitted through the glass-frit line to melt it and bond the substrates—Figure 14. Therefore, the device is completely protected from the outside moisture and oxygen, being all the degradation caused only by intrinsic factors mostly related to cell operation. In fact, a glass frit-sealed PSC displayed 15 months of stability (in ambient condition) with no efficiency loss. Surprisingly, the heat-affected zone during the laser emission was ca. 2 mm, and therefore, the sealing procedure did not affect/degrade the device active layers. Moreover, besides being totally scalable, this encapsulation process is also economical: sealing material low cost, low temperature required (65°C) and no need for additional current collectors. The devices were sealed at ambient atmosphere, but despite the presence of residual oxygen and water remained inside the device, no PCE loss was verified in any stress test.118 Again, it is important to highlight that these results were obtained for monolithic configuration and so residual water and oxygen inside the device may not damage the device.

After assessing the encapsulation techniques selected, the one that stands out is the method reported in this last publication. Laser-assisted glass-frit encapsulation is totally scalable and reproducible, the sealing material quantity required is minimized, the perovskite suffers no damaging during sealing, it can be used with any perovskite architecture, and the encapsulation is hermetic. In case, there are compounds in the PSC

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**Figure 13** Scheme of PSC encapsulation based on UV-curable epoxy edge sealing (A) with and (B) without paraffin.117 Copyright 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

**Figure 14** Illustrations of: (A) encapsulation procedure with glass-frits types identified (A, B and C) and (b) device after encapsulation.119 Copyright 2020 Royal Society of Chemistry
highly sensitive to moisture and oxygen, this encapsulation method can easily be used together with the atomic layer deposited alumina, and so the residual water and oxygen trapped inside the device will not affect those compounds. Instead, an inert chamber for device sealing can also be built, but this is a more complex and thus less attractive option. The substantial drawback is the possibility of lead leakage in case of glass breaking. This topic will be discussed later.

5 | UPSCALING

A PCE loss is inevitable when active area increases, namely from lab cells (~0.1 cm²) to large-area cells (~1 cm²) and modules (> 10 cm²). There are two main reasons responsible for the PCE drop in larger substrates. First, the uniformity and quality of the perovskite absorber layer deposited by typical deposition method—spin coating—decrease with cell dimension due to the centrifugal force. All the other methods are still not as good as spin coating. Second, since the cell is large, charge carriers will have to go through a longer path in the electrodes (TCO and BC), which increases the horizontal current flow resistance. The front-contact is the most critical because the resistance has to be minimized without compromising the substrate transparency; otherwise, PCE would also drop due to less photon harvesting. Moreover, for modules it has to be considered also the unavoidable dead areas of bus bars and interconnections.

In 2014, Di Carlo et al. produced the first solid state modules composed by 5 series-connected individual solar cells based on organometal halide perovskite MAPbI₃₋ₓClₓ, reporting a PCE of 5.1% for an active area of 16.8 cm². Since then, several works were published aiming the PSC upscaling, with topics regarding scalable deposition techniques for the production of uniform and pinhole-free perovskite films, the decrease in the substrate resistance (less studied) and optimization of modules designs. The largest PSM ever built was announced by Microquanta in October 2019. The PSM had a total area of 200 × 800 cm² and a PCE of 14.24%—Figure 15, but no information regarding the design or deposition methods was revealed. There is also investigation directed to flexible substrates, but they are not in the scope of this review. The fabrication of PSC under ambient atmosphere is also a pertinent topic towards the simplification and affordability of the manufacturing process at an industrial scale.

5.1 | Scalable deposition methods

To manufacture a Perovskite Solar Module (PSM) at an industrial scale, it must be adopted deposition methods accordant to that scale. As already stated, the most used method, spin coating, is the best for lab cells but has several issues regarding scalability. Fortunately, the variety of alternative methods for depositing the PSC layers is wide. The main parameters that must be taken into account are as follows: i) uniformity and quality of the layer produced, amount of wasted material; ii) safety; iii) complexity; and iv) energy required for the deposition. Perovskite layer deposition is the most challenging one due to the complexity on creating defect-free perovskite crystals. The other layers can be easily deposited in large substrates by solution, printing or evaporation processes, and high-quality layers are obtained without much efforts. A table of scalable techniques for depositing several HEL and EEL layers is presented in Appendix S3—Table S13. The PCE obtained with the different deposition methods is presented (ordered according to the respective PCE) in Table 9, and illustrations of some of those methods are represented in Figure 16. A more complete list is presented in Appendix S3—Table S14. Some of these methods—inkjet, blade, bar, slot-die and spray coatings—can be also assembled in a roll-to-roll installation, diversifying their application to flexible substrates and allowing a continuous production.

5.1.1 | Spin coating

In the spin-coating method, the solution is dropped in the middle of the substrate, which then rotates creating a centrifugal force that forces the solution to spread through its surface. The thickness of the film depends on parameters such as the wettability of the solution on the substrate, the
solution concentration and viscosity, rate of evaporation and angular speed. There are basically three variations of this method: antisolvent, one step and two steps. In the first variation, antisolvent is usually dropped during spinning, which causes a rapid and high-quality crystallization by solvent exchanging. This is currently the method allowing the best PCE, but it lacks reproducibility. The antisolvent can also be sprayed or used in a bath where the cells with the perovskite film are immersed. The one-step method is a simple spinning of the perovskite solution precursor, whereas in the two steps, the metal halide is spined first, and then the organic halide. Alternatively, the second step can be substituted by another method, such as dipping, low-pressure chemical vapour deposition, spray or vapour exchange. Another method consists of depositing metal halide and organic halide in separate substrates, join them and proceed with a close space sublimation—known as stamping. For all variations, the final perovskite film can also undergo a post-treatment to enhance crystal features, such as vacuum flash or vapour treatment annealing.

Despite the high values of PCE obtained at lab scale with spin-coating deposition technique, the amount of wasted material (ca 90%) along with the loss of uniformity for substrates larger than 10 × 10 cm² (due to the centrifugal force) keep this deposition method away from commercial use. Therefore, several improvements have been proposed and tested, such as solution processing at lab scale, dip-coating, blade coating, inkjet printing, spray coating, etc. These methods are often compared to evaluate their potential for large-scale fabrication. Herein, we present a summary of the PCE obtained with lab-size cells for different deposition methods, along with the configuration of the respective PSC. Methods are referent to the deposition of the perovskite layer and are ordered according to the PCE value.
from industrialization. As shown in Table 9, spin coating holds the best PCE, but other coating methods also allow high PCEs, rounding 20%. This is very promising; it means that the perovskite quality resulted from scalable depositions processes are approaching the high-quality crystals obtained by spin coating. Still, very good results were published with large-area spin-coated devices. Through the antisolvent strategy, Pengjun et al. fabricated a 196 cm² ETL-free PSC, which was then separated in 64 cells with average efficiency of 12.25% (decreasing ~4 percentage points from the centre to the corner). Concerning modules, Higuchi et al. fabricated a conventional n-i-p PSM with 354.45 cm² active area (35 cells in series) with a PCE of 12.6%. Han et al. fabricated a 100 cm² PSM with an astonishing PCE of 14.0%—Figure 17. For the HEL-free carbon-based devices, a good PSM is also reported with an active area of 52 cm² (divided in 10 strips) and a PCE of 10.2%. Also, Wu’s and his co-workers together with Nazeeruddin group reported an inverted PSM with an active area of 25.2 cm² (divided in 9 strips) that produced an outstanding PCE of 16.0%. Finally, a 10 × 10 cm² module with a PCE of 17.8% was recently fabricated by Bu et al., using a simple dynamic antisolvent quenching (DAS) process for providing crack-free and uniform large-area mixed-cation perovskite films.

5.1.2 | Inkjet coating

This method consists of propelling droplets of ink onto a substrate, allowing for an arbitrary design deposition at very low material consumption. It is a non-contact, fast, adaptable and very promising technique, which is already used in industrial production lines. Despite being the deposition method with the second highest PCE for lab cells (Table 9), there is not much publications about it—total of 55 articles since 2014 (data source: Scopus, December 2020; searched key words: perovskite solar cell inkjet). Even so, in January 2020 Panasonic announced a PSM with a huge active area of 802 cm² (total area of 30 cm ×30 cm), with a PCE of 17.9%—Figure 18. This astonishing result is a hopeful sign that PSM are really getting closer to commercialization.

Presently, the maximum PCE at lab size obtained for inkjet deposited perovskite is held by Eggers et al. in an inverted PSC—maximum PCE of 21.6% and maximum short-time stabilized PCE of 18.5%. A thorough optimization of the perovskite ink, deposition procedure and post-treatment (vacuum followed by thermal annealing) was accomplished; however, no PCE referent to a large cell was presented. On the contrary, Li et al. fabricated a large n-i-p mesoporous PSC with a PCE of 17.74%. The device had an active area of 2.02 cm², and the perovskite film obtained was fully uniform, compact and composed by large grains (>2 μm). This technique can also be used to uniformly deposit the perovskite precursor solution onto the porous stack of monolithic devices.

5.1.3 | Blade coating

This is a very simple technique in which a blade is used to spread a solution along a substrate. A high-quality perovskite film, with high surface coverage and large crystal domains, can be obtained by optimizing the following
parameters: gap between the substrate and the blade, ink properties, deposition speed, temperature of the substrate and the drying and annealing procedure. It was identified five very promising publications regarding bladed perovskite layers. First, Dai et al. fabricated a flexible PSM with 42.9 cm² active area that produced a PCE of 15.9%. The perovskite film quality was enhanced by NH₄Cl doping, whose effect is basically passivating defects caused by defective crystallization. Using the exact same architecture but in a rigid substrate and no doping, Deng et al. reported a very high PCE of 21.3% for a laboratory size cell and a PCE of 16.9% for a PSM module with an active area of 64.3 cm². A remarkable singularity of this publication is the high deposition speed of ~10 cm·s⁻¹, which is favourable for an industrial production line. To optimize the perovskite crystallization, the coating blade is followed by a nitrogen knife stream. An even higher PCE of 21.5% (lab-size cell) was published by Wu et al. with a very similar approach. No nitrogen knife stream was used, but instead the perovskite layer was doped with a bilateral alkylamine. A large cell with an active area of 1.1 cm² produced an exceptional PCE of 20.0%. The same authors published a very similar device but without HEL and with a different perovskite dopant: F4TCNQ. A lab cell achieved a PCE of 20.2% which is an outstanding value for a HEL-free monolithic device with ~60 cm² delivering a PCE of 12.9% (perovskite is doped with 5-AVAI)—Figure 19. Despite the high temperature annealing required, the three mesoporous layers (TiO₂ EEL, Al₂O₃ scaffold and carbon BC) are all cheap, scalable, stable and non-toxic.

5.1.4 | Slot-die coating

In the slot-die-coating method an ink is supplied to a slit in a fixed head. The ink passes through the slit and is deposited in a moving substrate, creating a thin film. Although this method is very similar to blade coating, it may require a longer optimization because the ink flow must also be carefully determined. Three Solliance partners reported an astonishing 144 cm² PSM composed by 24 strips, with a stabilized PCE of 13.8%. The EEL and HEL were also deposited by slot-die. A flexible 160 cm² PSM with a stabilized PCE of 10.1% is also reported. Slot-die coating can also be used to deposit the perovskite precursor solution in monolithic devices—Xu et al. reported a HEL-free monolithic device with ~60 cm² delivering a PCE of 12.9% (perovskite is doped with 5-AVAI)—Figure 19. Despite the high temperature annealing required, the three mesoporous layers (TiO₂ EEL, Al₂O₃ scaffold and carbon BC) are all cheap, scalable, stable and non-toxic.

5.1.5 | Other scalable deposition methods

The three aforementioned methods are the most promising regarding industrialization. Despite those, other methods are being pursued for allowing scalability. Bar coating is like blade coating, but it uses a bar instead of a blade. This method is infrequent, and the best reports published until now focus only on the n-i-p configuration, and use spin coating to deposit the other functional layers. The reported best lab cell has a PCE of 19.8%. For an active area of 1 cm², the PCE reported with this technique is 16.8%, while a PSM with an active and total area of 18.7 cm² and 25 cm², respectively, produced a PCE of 17.0%. In the spray-coating process, liquid droplets are dispersed from the nozzle onto the substrate. Although this method is very effective for depositing other layers, such as the TiO₂ EEL, it has been demonstrated not to be effective for depositing the perovskite layer. The reported maximum PCE reported for lab cells is ca. 17.5%, even with the other layers being deposited by fully optimized spin coating. This PCE drops to 15.5% for a PSM with an
Physical and chemical vapour deposition is usually performed under high vacuum, and the material sources have to be subjected to high temperatures to sublimate/react. Obviously, these methods are expensive due to the energy requirements and must then be avoided. Anyway, it should be highlighted the work of Luo et al., who fabricated a 41 cm² PSM with a PCE of 12.2%, and of Li et al., that achieved 18.1% in a PSM with 21.0 cm² active area. On the contrary, the pressure-processing technique is solvent- and vacuum-free and

| Device | Method | PCE / % | Active area / cm² | Configuration | Ref. |
|--------|--------|---------|-------------------|--------------|------|
| Large PSC | Spin coating | 20.5 | -1 | FTO/c-TiO₂/meso-TiO₂/TriC perov./spiro-OMeTAD/Au | 135 |
| | Blade coating | 20.0 | | ITO/PTAA/MAPbI₃/DAP/C60/BCP/Cu | 149 |
| | Physical vapour deposition | 19.0 | | FTO/TiO₂/SnO₂/PCBM/MAPbI₂/spiro-OMeTAD/Au | 160 |
| | Meniscus assisted | 18.2 | | FTO/c-TiO₂/[(FA,MA)Pb(I, Br)]/PTAA/Ag | 162 |
| | Inkjet coating | 17.7 | 2 | FTO/c-TiO₂/meso-TiO₂/MAPbI₃/ spiro-OMeTAD/Au | 145 |
| | Bar coating | 16.8 | -1 | ITO/SnO₂/Perovskite/spiro-OMeTAD/Au | 154 |
| | Dip coating | 15.4 | | ITO/NiOₓ/MAPbI₃Clₓ/PC₇₁BM/PEI/Ag | 163 |
| | Spray coating | 14.2 | | ITO/PEDOT:PSS/MAPbI₃/C60/BCP/Cu | 256 |
| | Monolithic | 11.7 | | FTO/c-TiO₂/meso-TiO₂/MAPbI₃/ZrO₂/CoOₓ/Carbon | 257 |
| small PSM (<7cm ×7cm) | Dip coating | 16.0 | 12.0 | FTO/ZnO-ZnS/meso-TiO₂/[(FA,MA)Pb(I, Cl)]/spiro-OMeTAD/Au | 252 |
| | Spin coating | 14.9 | 16.1 | FTO/SnO₂/TriC perov./spiro-OMeTAD/Au | 258 |
| | Bar coating | 17.0 | 18.7 | FTO/SnO₂/[(FA,MA)Pb(I, Br)]/spiro-OMeTAD/Au | 155 |
| | Physical vapour deposition | 18.1 | 21.0 | FTO/TiO₂/SnO₂/PCBM/MAPbI₂/spiro-OMeTAD/Au | 160 |
| | Spin coating | 16.0 | 25.2 | ITO/LiCoO₂/MAPbI₃/C60/BCP/Cu | 127 |
| | Pressure processing | 17.9 | 25.5 | FTO/SnO₂/[(FA,MA)Pb(I, Br)/spiro-OMeTAD/Au | 259 |
| | Spray coating | 13.9 | 36.1 | FTO/c-TiO₂/meso-TiO₂/MAPbI₃/ spiro-OMeTAD/Au | 161 |
| | Physical vapour deposition | 15.5 | 40.0 | FTO/TiO₂/MAPbI₃Clₓ/PTAA/Au | 158 |
| | Blade coating | 12.2 | 41.0 | ITO/SnO₂/TriC perov./SpIro-OMeTAD/Au | 159 |
| | Blade coating | 15.9 | 42.9 | ITO/PTAA/MAPbI₃/C60/BCP/Cu | 147 |
| | Blade coating | 14.7 | 47.0 | FTO/c-TiO₂/meso-TiO₂/MAPbI₃/ spiro-OMeTAD/Au | 151 |
| large PSM (>7 cm × 7 cm) | Spin coating | 10.2 | 52.0 | FTO/c-TiO₂/meso-TiO₂/MAPbI₃/Carbon | 141 |
| | Slot-die (monolithic) | 12.9 | 60.1 | TiO₂/ZrO₂/MAPbI₃+5-AVAI/Carbon | 153 |
| | Blade coating | 16.9 | 63.7 | ITO/PTAA/MAPbI₃/C60/BCP/metal | 148 |
| | Dropping (monolithic) | 10.7 | 70.0 | FTO/c-TiO₂/meso-TiO₂/ZrO₂/MAPbI₃+5-AVAI/Carbon | 260 |
| | Spin coating | 15.3 | 70.0 | FTO/c-TiO₂/meso+G-TiO₂/[(FA,MA)Pb(I, Br)/PTAA/Au | 261 |
| | Chemical vapour deposition | 9.3 | 91.8 | FTO/SnO₂/C60/TriC perov./spiro-OMeTAD/Au | 255 |
| | Spin coating | 14.0 | 100 | FTO/PAH/SnO₂/TriC perov/spiro-OMeTAD/Au | 126 |
| | Slot-die coating | 13.8 | 144.0 | ITO/SnO₂/[(Cs,FA)Pb(I, Br)]/spiro-OMeTAD/Au | 152 |
| | Spin coating | 12.6 | 354.0 | FTO/c-TiO₂/meso-TiO₂/MAPbI₃/ spiro-OMeTAD/Au | 140 |
| | Printing process | 11.7 | 703 | | 262 |
| | Inkjet coating | 17.9 | 802.0 | | 19 |
has a similar performance: a 36 cm² PSM produced PCE of 13.9%. Other methods include meniscus-assisted deposition, dip coating and electrodeposition but with no relevant publications in field.

### 5.1.6 Summarizing the scalable deposition methods

The most relevant results regarding large PSCs and PSMs fabricated with the aforementioned deposition methods are summarized in Table 10. Solution-based processes are the most promising for depositing the perovskite layer. Vapour deposition processes, despite not producing high PCEs, they are also highly energy-consuming. Other very promising deposition methods are blade coating, inkjet and slot-die, both for conventional and monolithic devices. Besides producing high PCEs, they allow for a continuous production assembly. Inkjet is particularly appealing due to its versatility, high speed and waste minimization. Still, these solution processes may arise problems related to the toxicity of the solvents and atmosphere restrictions during deposition. Regarding stability, most of the discussed works use a simple MAPbI3 perovskite, but it may be worth to replace or add the FA cation and bromide anion to enhance thermal and long-term operational stability, respectively, and caesium cation to increase moisture resistance. Alternatively, a dopant can be added instead.

### 5.2 Electrical resistance of the substrate

PSCs, as well as other technologies such as touch screens, smart windows, LCD, OLED and other solar cells, heavily rely on the use of TCO-coated glass substrates. The metal oxide itself is usually not conductor, but the doping provides this capacity to the material. As mentioned in Chapter 3.1, the two most used TCOs are FTO and ITO. FTO features best thermal resistance and lowest price, while ITO has higher transparency and lower roughness. For minimizing energy loss, the TCO conductivity must be maximized. Galagan et al. confirmed by simulation that the substrate sheet resistance limits the maximum active area of an efficient perovskite solar module (PSM). For instance, the width of a cell deposited on a 10 Ω·sq⁻¹ substrate should be no more than 7 mm, whereas for a 60 Ω·sq⁻¹ substrate, the maximum width is 3 mm. Experimental data confirmed these simulation results. The current minimum ITO and FTO sheet resistances are 3 and 7 Ω·sq⁻¹, respectively, which is still a high value for a large PSC.

A strategy to decrease the TCO resistance is to incorporate thin metal lines in the substrate (called fingers) for preferential charge extraction. If built in a PSM, the fingers will drive the charges to bigger collective conductive lines, called bus bars. This strategy may be risky, though, because the metal thin lines may create short circuits in PSC due to the active layers’ low thickness and coating constrains on the metal grid. Metal lines also increase the fabrication costs and the weight of the device. Wilkinson et al. developed a complete simulation study about this strategy. By using an optimized metal grid on the substrate, they recorded a potential PCE of 21% for three different cell designs with an area of 200 cm². Experimentally, a group of researchers led by Hambsch applied an aluminium grid in a 5 cm × 5 cm cell, achieving a PCE of 6.8%—Figure 20. The perovskite wetting properties on the metal lines were enhanced by forming an alumina layer atop aluminium lines (through UV-ozone plasma exposure). Kim et al. produced a grid connected module with a certified 12.1% PCE, corresponding to a n-i-p device with 16 cm². A better perovskite quality was achieved by spraying the antisolvent at the spinning perovskite film.
Alternatively, instead of decreasing the FTO sheet resistance, Chang et al. patterned the FTO (hexagonal pattern of inverted truncated cones) to decrease light reflection, and consequently boost the light absorption—Figure 21. The patterned FTO also increased the interfacial contact area of the FTO/EEL and EEL/perovskite, enhancing the charge transfer efficiency. With this FTO adaption, PCE enhanced ca 25%.169 Instead of having a transparent substrate, it is possible to reverse the PSC orientation—transparent BC and opaque substrate. For instance, Abdollahi et al. used a copper foil as substrate for an inverted PSC, and transparent silver nanowires for BC. PCE obtained is not high—12.80%—but this work could be a starting point for further investigation on this approach.170

Another transparent conductive material used is AZO-coated glass substrate (minimum sheet resistance of 10 Ω·sq⁻¹).171 In this range of resistivity, there is still other metallic materials such as TiO₂/ultrathin Ag/TiO₂ electrode deposited by magnetron sputtering. On a flexible substrate, it displays a sheet resistance of 9.5 Ω·sq⁻¹ and a transmittance of 82%.172 ITO keeps being the best substrate for highly efficient PSM—minimum resistivity and maximum transparency. It is also used in flexible substrates,146 but its high price and thermal sensitivity is a great commercialization barrier. Zhang et al. minimized the PCE loss caused by the annealing (at 500°C) damage on ITO by optimizing the ITO thickness and the cell geometry—Figure 22.173 Even with this impressive minimization of the conductivity and transmittance loss, the final sheet resistance is still high for large substrates (20 Ω·sq⁻¹), and thus, it may be worth to use the cheaper FTO instead. Further research is still needed in this area, with the aim of obtaining a substrate that is highly conductive and transparent, but cheap and compatible with the PSC structure and fabrication.

5.3 | Module fabrication

Due to the PCE reduction for large cells, it is preferable to fabricate modules composed by several small interconnected sub-cells. The PSM should be designed to maximize the active area and PCE, and the manufacturing complexity and series resistance of the interconnections should be minimized. The dead area is quantified by the geometrical fill factor (GFF), which corresponds to the active area divided by the total area of a module—usually, PSMs present a GFF close to 95%.174 PSM are usually built in a
monolithic structure—Figure 23. It consists of connecting many sub-cells in series by a sequence of three laser scribings in a large cell—P1, P2 and P3 scribes. The sub-cells share a common glass substrate coated with a TCO. First, the P1 scribe lines remove the TCO without interfering with the glass. The P1 scribe electrically isolates segments that are going to be the sub-cells. Then, all the active layers are deposited above all the substrate and P2 scribe is made just a bit further to the P1, removing the active layers without removing TCO. A partial removal of the ETL/HEL at the TCO interface affects significantly the module performance and must be avoided.175 Also, the concentrated heat during P2 scribing may induce an explosive boiling and PbI₂ formation. These effects can be mitigated through the use of picosecond laser pulses. This ablation mechanism also leads to a favourable morphology, that is steep edges.176 It was also reported that 532 nm is the optimal wavelength for removing the active layers without damaging the FTO. Furthermore, P2 scribing can also be achieved by illuminating the substrate side—perovskite is preferentially heated, causing a micro-explosion assisted lift-off mechanism. Compared with the film side illumination method, this method results in a significantly reduced scribing threshold, that is narrow dead zone width but also large portion of electrical contact width.177

Back-contact is then deposited, filling the P2 path which connects the sub-cell to the substrate of the next sub-cell. The contact between the BC material and the active layers at the P2 path may cause undesired recombination or metal BC diffusion into the active layers. To avoid that, Bi et al. proposed the implementation of a diffusion barrier—tri-s-triazine-based graphitic carbon nitride nanosheets injected by a robotic syringe. This strategy successfully reduced the ions interfacial diffusion by 10³–10⁷ times in magnitude, but also increased the dead area and the fabrication complexity.178 Finally, P3 scribing separates completely the sub-cells since it removes the BC and the active layers, leaving the TCO as the only path for the charges to travel from the first cell to the second. These three scribes must be narrow and as close as possible to each other to minimize the dead areas due to interconnections. The output voltage is the sum of the voltage of each individual cell, but the current and consequently the PCE are limited by the worst performing one. Higher currents can be achieved by parallel interconnecting multiple modules, which will also prevent one damaged cell to ruin the entire module power production.

The first perovskite solar module was published in 2014 by Aldo di Carlo’s team.119 The PSM with a PCE of 5.1% was composed by 5 interconnected sub-cells, with a total active area of 11.52 cm². Since then, several other works concerning PSM fabrication have been published. It is not possible to define the best design for a PSM since it is dependent on layers properties, such as TCO resistance, perovskite deposition restrictions and back-contact features. However, a simple and effective design for a start is a simple square module divided into long strips. In this way, current losses associated with substrate resistance are minimized without compromising much the active area: charges in the substrate of a sub-cell just have to cross the width of the strip to reach the back-contact of the following sub-cell. With this approach, the only geometrical parameter that needs optimization is the sub-cell width. Even so, each PSC configuration has its own ideal PSM design that can and should be fully optimized through simulation software-like LAOSS from FLUXiM.179

5.4 | PSC fabrication under ambient atmosphere

As aforementioned, PSC inner components, especially the perovskite layer itself, are highly sensitive to the ambient atmosphere (presence of oxygen and relative humidity level). This condition contributes to the utmost need for final encapsulation but also means that the device fabrication must be performed under inert atmosphere. However, to build an industrial plant to sequentially deposit the perovskite device layers maintaining an inert atmosphere is quite complex and costly. Hence, the selection of moisture and oxygen resistant layers is a step towards the simplification and cost reduction of the manufacturing process. For the perovskite layer, this means doping or engineer the perovskite crystallization to hinder the occurrence of degrading reactions catalysed by water, as already discussed. The most promising works
| Device structure | Functional layers deposition method | Perovskite configuration | active area / cm² | PCE / % | RH / % | Ref. |
|------------------|-------------------------------------|--------------------------|------------------|---------|-------|------|
| Antisolvent spin coating | | | | | | |
| FTO/c-TiO₂/meso-TiO₂/perovskite/spiro-OMeTAD/Au | Spin coating | FAI, Csl, PbBr₂, PbI₂ + DMF, DMSO | 0.25 | 20.8 | 15–25 | 180 |
| FTO/NO₃/perovskite (prenucleation)/PMMA/PCBM/PPDIn6/Ag | Spin coating | PbI₂, MAI + DMF, DMSO (increased concentration) | 0.1 | 19.5 | 20–60 | 181 |
| FTO/c-TiO₂/modified TiO₂/perovskite/spiro-OMeTAD/Ag | Spin coating | CH₃NH₃PbI₃ | 0.09 | 19.62 | amb | 182 |
| ITO/PFAA/MAPbI₃/PTzDPBTz/C₆₀/PEI/Ag | Spin coating | PbI₂, MAI + DMF, DMSO | 0.12 | 19.19 | 72 | 183 |
| FTO/c-TiO₂/perovskite/spiro-OMeTAD/Au | Spin coating | PbI₂, MAI, NH₄SCN + DMF, DMSO | 0.12 | 18.75 | 30–50 | 184 |
| FTO/c-TiO₂/perovskite/spiro-OMeTAD/Au | Spin coating | PbI₂, ZnO NPs + DMF / MAI + IPA | 0.17 | 18.34 | 55–65 | 185 |
| One-step spin coating + AX cation dipping | | | | | | |
| FTO/c-TiO₂/perovskite/spiro-OMeTAD/Au | Spin coating | PbI₂, MAI + DMF, DMSO / MAI + IPA | 0.1 | 19.38 | 60 | 186 |
| One-step spin coating | | | | | | |
| FTO/SnO₂/perovskite/spiro-OMeTAD/Au | Spin coating | PbI₂, ZnO NPs + DMF / MAI + IPA | 0.045 | 16.59 | -70 | 187 |
| ITO/CPTA/VACl/perovskite/spiro-OMeTAD/MoO₃/Au | Spin coating | PbI₂, MAI + MAAc | 0.12 | 17.56 | 60–80 | 188 |
| FTO/c-TiO₂/meso-TiO₂/perovskite/spiro-OMeTAD/Au | Spin coating | PbI₂, MAI (excess) + DMF, DMSO | 0.13 | 18.26 | -50 | 189 |
| Screen printing | | | | | | |
| FTO/c-TiO₂/meso-TiO₂/meso-ZrO₂/perovskite/carbon (monolithic) | Screen printing | PbI₂, PbBr₂, Csl, CsBr + DMF / FAI + IPA | 0.16 | 8.47 | amb | 190 |
| Ultrasonic spray coating + antisolvent bath | | | | | | |
| ITO/SnO₂/perovskite spiro-OMeTAD/Au | Spin coating | FAI, PbI₂, MAI, PbBr₂, Csl, MACl + DMF,NMP, DMSO | 0.8 | 14.14 | amb | 246 |
| Ultrasonic spray coating | | | | | | |
| FTO/c-TiO₂/perovskite/spiro-OMeTAD/Au | Spray/spin coating | PbI₂, MAI + DMF | 0.0671 | 13.53 | <50 | 263 |
| Blade coating | | | | | | |
| FTO/In₂O₃/CH₃NH₃PbI₃/perovskite/spiro-OMeTAD/Au | Blade coating | PbI₂, MAI + GBL | lab | 13.97 | 40–50 | 264 |
| FTO/NiO/perovskite/PC₆₁BM/BPC/Ag | Spin coating | PbI₂, MAI + DMF, DMSO | 0.1 | 13.83 | -45 | 265 |
| ITO/NiO/perovskite/PC₆₁BM/Ag | Blade coating | PbI₂, MAI + DMF, DMSO | 0.09 | 10.92 | -40 | 266 |
| Injet infiltration | | | | | | |
| FTO/c-TiO₂/meso-TiO₂/meso-ZrO₂/perovskite/carbon (monolithic) | Spray/screen printing | PbI₂, MAI | 0.16 | 8.47 | amb | 146 |
| Slot-die | | | | | | |
| ITO/FrGO/perovskite/PC₆₁BM/BCP/Ag | Slot-die | PbI₂, MAI, CHP + DMF, DMSO | 0.1 | 12.56 | amb | 267 |
| ITO/PEDOT:PSS/perovskite/PCBM/Ca/Al | Spin coating | PbI₂, MAI, NH₄Cl + DMF | 0.1 | 15.57 | amb | 193 |
about fully ambient air processed PSCs are presented in Table 11; a more complete table is presented as supporting information— Appendix S3— Table S15.

The best performing PSC fully fabricated under air atmosphere has a PCE of 20.8%. The device reported by Singh and Miyasaka is a typical mesoporous tri-cation perovskite, deposited by the antisolvent spin-coating method without any adjustment on the procedure to avoid PCE loss due to water presence. However, the RH range defined was not truly realistic (only 15–25%) as RH can easily rise up to 80% on a normal winter day. Still regarding antisolvent spin-coating deposition, other works have reported PSCs with PCE higher than 19% in which RH is ranged between 20 and 72%. First, Zhang et al. used a more concentrated perovskite precursor solution and adapted the antisolvent deposition method as presented in Figure 24— prenucleation method, though, this strategy would be quite difficult to upscale. Second, Seyed-Talebi modified the ETL of TiO2 to optimize its porosity and consequently enhance perovskite infiltration and crystallization, which resulted in a more water-resistant perovskite layer. Briefly, removable carbonaceous sphere templates were used to fabricate TiO2 hollow spheres that were incorporated in a paste and deposited by spin coating— Figure 25. Finally, Chang et al. minimized the defects at grain boundaries and/or the film surface by adding PTzDPPBTz as passivating layer, which resulted in a great PCE and stability even at a RH of 72%. Apart from these works, Angmo et al. also demonstrated that NH4SCN additive lowers perovskite defect density (NH4+ and SCN− passivate defect traps), resulting in a PCE of 18.8% even with a RH of 30–50%.

For the two-step spin-coating deposition method, three interesting strategies were proposed: dope PbI2 solution with ZnO nanoparticles; dope PbI2 solution with KSCN; and add n-butyl amine and n-butanol to the PbI2 and MAI solutions, respectively. ZnO nanoparticles act as nucleation sites for crystal growth and also create PbI2 smaller domains inside the pinholes, filling them and creating a uniform film— Figure 26. Regarding KSCN additive, alkaline cations such K+ also act as nucleation sites like the ZnO nanoparticles and facilitates the grain growth, enhancing the grain size and the perovskite morphology. Additionally, the anion of the lead precursor selected in this paper, SCN−, has much stronger interactions with Pb2+, resulting in an increased moisture resistance. Chloride anion has also this effect, and therefore, it is also used to improve air stability. Finally, adding a small amount of a strong Lewis base (n-butyl amine) and a low hydrophilic solvent (n-butanol) to the PbI2 and (MAI + MACl) mixture, respectively, makes the crystallization less dependent on the indoor humidity. Nevertheless, instead of dripping MAI solution during spin coating, Cheng et al. dipped the device with

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**FIGURE 24** Scheme of the procedure to fabricate perovskite films through the conventional and prenucleation methods.

**FIGURE 25** Field Emission Scanning Electron Microscopy images of the (A) removable carbon spheres and (B) TiO2 hollow spheres. Copyright 2019 Elsevier Inc. All rights reserved.
PbI₂ in an MAI solution, with consequent **air-knife recrystallization** - Figure 27. Besides resulting in a more uniform and denser perovskite layer, these two steps can likely be upscaled.¹⁸⁹

Concerning one-step spin coating and using *methylvammonium acetate* (MAAc) as the perovskite precursor solvent, a PSC fabricated under 30–80% RH reached 20% PCE. The high quality and pinhole-free perovskite layer resulted from the fast liquid-to-solid transition of perovskite through a deformed perovskite intermediate structure. This strategy is particularly attractive given its simplicity, effectiveness and the solvent non-hazardous nature.¹⁹⁰ Other strategies include the use of **carbon-graphite-Cu:NiO** additive (passivates perovskite's trap states and suppresses recombination at the interfaces)¹⁹¹ and the use of **MAI in excess** (promotes grain growth).¹⁹² The following air-processed PSC presented in Table 11 were fabricated through scalable processes: screen printing, ultrasonic spray coating, blade coating, inkjet infiltration and slot-die. The obtained PCEs are visibly lower, meaning that an optimization of the strategies mentioned for large-scale deposition is essential. From all the presented strategies, the ones more likely to be adjusted and succeed in a large scale is the methylammonium acetate perovskite solvent, air-knife recrystallization and NH₄SCN or NH₄Cl additives. Still, some...
attempts were already reported such as the NH₄Cl¹⁹³ and MACl¹⁹⁴ incorporation in the perovskite precursor solution deposited by slot-die and ultrasonic spray coating, respectively. The addition of NH₄Cl resulted in an enhanced perovskite film quality and a PCE of 15.57% (lab-size cell). The incorporation of MACl on the perovskite recipe had even better results: PCE of 18.5% in a lab cell and 15.07% in an active area of 1 cm².

6 | ENVIRONMENTAL IMPACT

Before being commercialized, any technology has to be assessed in terms of its potential environmental impact through a life-cycle assessment. This holistic assessment analyses all energy and material inputs and environmental releases of each step of the technology production and operating life, starting from the extraction/synthesis of the raw materials until the technology end-of-life treatment. Typically, cradle-to-grave assessment is divided into five stages: (1) raw material extraction, (2) synthesis of starting products, (3) fabrication, (4) use and (5) decommissioning - Figure 28.¹⁹⁵ Here, Stages (1) and (2) are not analysed because most of the materials needed for PSC production are already used in an industrial scale for other applications, and thus, their environmental impact was already determined. Regarding Stages (3), (4) and (5), a rough outlook is performed to assess which are the most critical environmental aspects of the PSC technology and which solutions were already proposed to decrease the environmental impact.¹⁹⁵

6.1 | Fabrication stage

Fabrication of a perovskite solar device is a complex process. It includes the sequential deposition of several high-quality thin films that may require a controlled atmosphere and post-treatment steps. Factors that may affect the environment, directly or indirectly, is the material waste and energy expense in the deposition processes (e.g. vacuum requirements, high temperature or controlled atmosphere), the toxicity of the materials and solvents and safety measures to apply during assembling.

Starting with the deposition methods, they can be divided into physical and chemical techniques. The physical coatings used in PSCs consist mainly in evaporation and sputtering, where a target is stressed by high temperature or by energy electrons or ions, respectively, under high or medium vacuum. Despite producing films with great quality, they are highly energy-consuming and thus with higher environmental impact. PSC layers deposited by these methods are basically the metal and conductive oxides BCs. Chemical deposition used in PSC includes a larger number of techniques: spincoating, dip coating, electrochemical deposition, spray pyrolysis, CVD, plasma-enhanced CVD and ALD. Spin coating is undoubtedly the method that produces the best quality films, but the amount of material wasted is huge (>90%) and its applicability is limited to lab-size devices.⁶⁷,¹⁹⁶ Spray pyrolysis, CVD, plasma-enhanced CVD and ALD are highly energy demanding due to the low vacuum or/and the high temperature required. The remained 6 methods are certainly less energy demanding and then eco-friendlier: dip coating, screen printing, slot-die, doctor blade, inkjet and electrochemical deposition.

Some layers also require a long annealing step at high temperature (~450°C), like the inorganic selective layer of TiO₂, SnO₂, and NiO and the spacer layers ZrO₂ and Al₂O₃ used in monolithic devices. Despite the highly energy demand post-treatment, the mentioned materials are stable, relatively cheap, very efficient on extracting selective charges, and easily upscaled. Fortunately, there are already successful strategies to lower the respective annealing temperature.⁹⁶,¹⁹⁷,¹⁹⁸ Regarding the controlled atmosphere, all the fabrication process must be designed taking this factor into account. Industrially, it is very challenging to build large inert atmosphere facilities for perovskite fabrication and its operation is also costly. The most atmospheric sensitive layer is the perovskite itself, mainly due to the moisture-induced degradation.⁷¹ Obviously, its replacement is not possible, but the degradation mechanism can be mitigated using especially developed perovskite formulations, as indicated in Chapter 4.2.
**Chemicals toxicity** is also a very important aspect concerning the environmental evaluation. Particularly, lead content in the perovskite absorbing layer is of major concern: inside the human organism, lead ions mimic essential elements such as Ca, Zn, and Fe, which impair the functionality of enzymes and receptors from the liver, kidney and nervous tissue, causing serious damages. In case, there is a lead leak from the panel, and this lead reaches the soil, it will be absorbed by the plants, and consequently, it may enter into the food cycle ten times more efficiently than lead contaminants resultant from other human activities. Furthermore, lead salts are highly soluble in water and thus can be transported by the groundwater causing a serious impact on public health.\(^{21,199}\)

However, it represents a colossal challenge to fabricate efficient and stable PSCs without lead. The best candidate to replace lead is tin (Sn), given its similarities to lead. The bandgap of MA\(_3\)SnI\(_5\), FA\(_3\)SnI\(_5\), and CsSnI\(_3\) is 1.20, 1.41, and 1.3 eV, respectively, which is very close to the optimal range (1.3–1.4 eV). These narrow bandgaps result in high current densities, similar to Pb-based devices. However, the potential at open circuit is about 0.5 V, resulting in PCEs lower than 10%. Stability is also significantly worse. Germanium and bismuth can also be used to replace lead; however, their performance is even poorer than Sn-based devices.\(^{200}\) Basically, it was not yet proposed a successful lead replacer. Nevertheless, the amount of lead in a PSC per area is not that high comparing to other already commercialized technologies, such automotive-type lead-acid batteries: ~60 wt.%.\(^{20}\) It can be estimated that a 200 nm thick MAPbI\(_3\) film with one square metre area contains ~300 mg of lead. Regarding legislation about this topic, Europe defined in 2011 and consolidated in 2020 that the maximum lead concentration tolerated in electrical and electronic equipment is 0.1 wt.%.\(^{201}\) However, this directive also includes about 20 exceptions (directed to applications related to medical devices and monitoring and control instruments) that were exempt from this regulation. Moreover, in Article 2 (4.i) it is mentioned that ‘This Directive does not apply to: photovoltaic panels intended to be used in a system that is designed, assembled and installed by professionals for permanent use at a defined location to produce energy from solar light for public, commercial, industrial and residential applications’, which includes the perovskite solar devices.\(^{201}\) Furthermore, a study published in 2017 estimated the toxicity impact in humans and environment caused by lead iodide present in perovskite-based tandem solar cells. Later on, these authors extended this study to non-renewable energy sources. They concluded that the environmental burdens caused by perovskite-based solar cell fabrication process are less severe as the ones caused by using non-renewable energy sources to produce the same amount of energy. The calculations were based on a lead iodide mass balance, and in case of uncertain data, the maximum amount of lead was considered so as to obtain the worst-case scenario. Regarding PSCs, it was taken into account: i) lead emitted to the atmosphere by reaction with polar solvents; ii) leaks to the surroundings of industrial soil during PV panels manufacturing; iii) lead leaked to surface freshwater at the panels dismantling; and iv) lead emitted by its final incineration or washed at the landfill.\(^{202}\) Though, instead of removing lead, other alternatives are as follows: i) minimize the lead emissions and waste at its manufacturing; ii) minimize its leakage risk at the panel life by an exceptionally resilient encapsulation; and iii) develop an efficient method to recycle lead and, if possible, reuse the TCO substrates. These topics are discussed further ahead.

Other toxic components used in the fabrication stage (but not present in the final device) are solvents such as DMF, GBL, NMP, HMPA, chlorobenzene and toluene. The perovskite solvents (the first 4) are the most worrying because their high solubility in water that enhances the bioavailability and the risk of absorption either by oral ingestion or by dermal contact. DMF is particularly toxic: it is readily absorbed either through the skin, inhaled or ingested, is a potent liver toxin and may cause other symptoms such headache, dizziness, nausea and vomiting.\(^{203}\) Whenever possible, these solvents must be replaced by greener ones. Anyway, rigorous handling safety measures have to be imposed in this stage as well as in the following to avoid leakages and contaminations either by hazardous solvents or by heavy metal compounds in the solid, liquid or vapour form.\(^{195}\)

### 6.2 | Use stage

Passing to the following stage—use—the main concern is the risk of break due to certain mechanical stress like hail impact or during an earthquake, and consequent leakage of lead (dissolved in rainwater) for the surrounding environment.\(^{195}\) It is said that lead dissolved in the rainwater is strongly absorbed by the soil, being ready immobilized in the first few centimetres.\(^{204}\) However, if this contaminant ever reaches the water underground, it can be taken to other locations, increasing the hazard for public health. The challenge here is to **prevent lead leakage** from a broken panel. Jiang et al. proposed the use of a self-healing epoxy resin as thin-film sealant that would resist to mechanical impacts and thus reduce the lead exposure to atmospheric conditions.\(^{24}\)

Three encapsulation methods were specifically studied to address possible lead leakage. The so-called method D consists of first sealing the bottom (BC side) edges with UV-curable resin, which also fixed the module to a bottom...
glass cover, and then sandwiching a thin thermocrosslinking epoxy resin between the perovskite solar module substrate and a top glass cover. This sealing method allowed a reduction of 375 times the extracted lead by simulated sunlight heated rainwater compared with the encapsulation based on just UV-curable resin on the edges. If the thermocrosslinking epoxy resin suffers a cut, it has the capacity to fix the slit in case it is subjected to a temperature higher than its glass transition temperature (~ 45°C)—a microstructured resin is formed, filling the slit. This heating can easily be produced by the sunlight, and if the temperature increases further to 85°C, the film will heal even faster, with no degradation. However, during the resin healing time (4 h for 45°C and 1 h for 85°C), lead is still exposed to the atmosphere and lead leakage may occur.24 Instead of containing the lead inside a broken panel, a lead-absorbing material could be somehow incorporated in the device to further minimize the risk of leakage. The lead sequestration is instantaneous and there is no PCE loss during encapsulation, looking therefore more appealing than the self-healing resin. Devices with this material coated on each glass covers retained more than 96% of the lead leaked after a severe damage. On the back side, it was used 0.45 mm of EDTMP-PEO as lead absorbent. This material was first deposited by doctor blade on another substrate and then laminated above the perovskite device. On the front side, the lead absorbent consists of 2.4 µm of DMDP deposited by spin coating on the back side of the perovskite substrate.23 Nonetheless, DMDP is relatively expensive (Appendix S1—Table S10). If required a maximum lead protection, these two methods could be merged.

Fire can also induce the lead release. This would cause the emission of toxic fumes that would be easily spread and absorbed by the humans via inhalation. Mitigating or even eliminating this danger is a difficult task. Babayigit et al. exposed tandem Si/perovskite modules to fire (temperature around 760°C) and concluded that the high temperature causes the formation of PbI₂. Afterwards, part of it was evaporated and the other part was converted into lead oxides that were totally absorbed by the encapsulation glass.205 Still, a complete investigation about the consequences of inhaling heavy metal-containing fumes is still indispensable to understand the PSC potential hazards and the correct measures to take in case of the occurrence of that event.

6.3 Decommissioning stage

Lastly, the decommissioning stage. An ideal decommissioning would involve the safe removal of the panel from its working place, the lead and the TCO substrates recycling and finally their reuse to manufacture new perovskite solar panels. Despite being a greener option, it is important to recycle lead and TCO because of their high toxicity and price, respectively. Fortunately, there are already procedures for recycling lead and TCO through simple solvent treatments followed by purification. Certainly, these procedures would have to be adapted according to device design and encapsulation method, but this stage is probably the least environmentally problematic. A very simple method was proposed by Augustine et al.; these authors submerged a n-i-p conventional device in a potassium hydroxide (KOH) aqueous solution and succeed to remove all layers within 5 min—Figure 29. The TCO substrates suffer no damages and can be reused for fabricating new cells.25 The challenge then would be to separate the extracted compounds from the KOH solution for allowing their reutilization.

![Figure 29](https://example.com/fig29.jpg)
Huang et al. followed a similar approach and succeed to remove the BC, HEL and perovskite layer from a p-i-n conventional PSCs with DMF, and then reused them and the old TiO2 layers for fabricating a new PSC.206 The PCE of the new device, produced from the extracted of the original one and named second device, dropped 10%, while the PCE of the third device dropped 6%. Alternatively, Binek et al. designed a procedure to remove each layer separately, so as to ease the recovery and reuse of each compound. Basically, first the metal BC was removed with scotch tape, and then, the HEL, the perovskite layer and the EEL were removed using a bath of chlorobenzene, water and DMF, respectively. These authors calculated that a 70 dm2 perovskite film yields ca 600 mg of PbI2 with very small amount of impurities, which can be reused to fabricate ca 2 dm2 of perovskite film. They assigned this low yield to the waste of perovskite precursor solution at the spin-coating process.207 The three cited publications focus just in conventional n-i-p PSC. Certainly, these procedures can also be adapted for inverted PSCs by selecting different solvents according to the materials used for each layer. Recycling monolithic devices may require a different methodology because their structure is fairly different from the conventional PSCs.

7 | OUTLOOK

This review aims at to guide scientists who are looking to develop more efficient, stable and cost-effective large PSC devices. Thus, after this exhaustive review concerning perovskite solar cells power conversion efficiency, costs, stability, upscaling and environmental impact, the most relevant findings are now holistically analysed. Starting with the substrate, the best transparent conductive oxide-coated glasses are FTO and ITO; ITO is more expensive and thermal sensitive, but also more conductive and transparent. The FTO high electrical resistance can be mitigated by incorporating metal thin lines. However, results obtained by this approach are not very promising.167 Thus, currently it is preferable to build a PSM made of small strip cells. TCO can also be patterned to increase its contact area with the EEL and light reflection decrease; however, this additional step would increase the fabrication complexity and cost.168 In any case, the substrate can be reused after the PSM lifetime by a simple and environmentally friendly process, which would decrease the long-term cost and the environmental impact of a module.25

The HEL is the layer with a wider range of possible materials (as supporting information it is presented the price of 28 possible HELs). Some of the most used HELs are unstable from the operation point of view and very expensive (>250 €/g), such as spiro-OMeTAD, PTAA P3HT, poly-TPD, P3CT-Rb, TFB and MPA-BTTI. Although their instability can be mitigated using dopants, such as Zn-TFSI, on spiro-OMeTAD,208 this increases fabrication protocols and consequently final costs. There are other cheaper HEL displaying high stabilities and high efficiencies (PCE >20%), like NiO2 for the p-i-n configuration, and CuSCN, CuPc, PDDO2, OMe-TATPyr and PHPT-py for n-i-p configuration. Furthermore, both NiO2 and CuSCN can be deposited by spray without compromising the PCE; CuSCN uses nitrogen as carrier gas and propyl sulphide as solvent,209 while nickel acetylacetonate is used to fabricate the NiOx layer with air as carrier gas.92 A protective interlayer, such as of rGO, can also be added to avoid unwanted side reactions at the interface between the HEL and the metal BC.80 Concerning the environmental impact, NiOx usually needs a high temperature sintering step at 500°C, but, fortunately, when doped with 1% at strontium, the annealing temperature is only 235°C for 45 min and keeps the PCE >20% even with a lower thickness of 20 nm. Strontium doping also enhances PCE and stability.198 On the contrary, a soft post-treatment is needed for the spray-coated CuSCN (80°C for 3 min). Anyway, the carbon-based n-i-p devices work well without any HEL, which is simplifies the fabrication process.

The materials available for using as EEL are fewer (20 presented in the supporting information). For n-i-p devices, the commonly used EEL is also affordable and stable—TiO2. When exposed to UV light, TiO2 induces the PSC degradation, but this drawback can be easily addressed with a UV cut filter.71 Usually, the highest PCEs are achieved with a double EEL—a compact and a mesoporous layer—but for an industrial scale, the simpler the architecture the best. Moreover, it was already reported a planar n-i-p device with 30 nm thick TiO2 deposited in ambient atmosphere conditions sintered under mild conditions—150°C for 30 min—that produced a PCE of 21.8%. This approach is also easily scalable.29 Other very efficient, stable, affordable and scalable EEL materials for n-i-p devices are SnO2, TMAH, ZnO, WO3 and 2D SnS2. For the p-i-n configuration, the majority of the identified materials are very expensive: PCBM,35,45,46 C60SAM, PDTzTI and PF—the majority of them costs more than 800 €/g. The material with the highest cost-effectiveness is C60. Although its usual deposition process is high energy-consuming (thermal evaporation under high vacuum), it is scalable, solvent-free, very efficient at extracting charges and produces high quality and thin films (30 nm). Moreover, when inside a vacuum chamber, a protective layer of 5 nm of BCP can be deposited after C60 (to mitigate the metal diffusion from the back-contact to the device inner layers) without breaking vacuum. Several works reported this double EEL as very efficient and stable, even with a metal BC-like copper. Still, there are other...
cheaper protective layers, deposited by less energy intensive scalable processes, such as ZnO and AZO.

In what concerns the **back-contact**, usually it is used gold for n-i-p PSCs and silver, aluminium or copper for p-i-n PSCs. Despite being very efficient at extracting charges, they may diffuse into the perovskite device inner layers hindering PSC performance. Moreover, their deposition is energy intensive, and gold and silver are also expensive. Fortunately, for the n-i-p configuration, very good results were obtained with carbon-based BC. A PCE of 19% can be achieved with a low-cost, stable and non-toxic carbon back-contact deposited by doctor blade.\(^{59}\) Regarding the p-i-n configuration, copper is a good choice since it is a cheap metal and can reach a PCE of 22.5%.\(^{210}\) In case the EEL and passivation layer are deposited by thermal evaporation, copper can be deposited afterwards without breaking the vacuum, which minimizes the energy requirement. Furthermore, several stability works present very good results using three sequential evaporated layers: C60, BCP and copper (e.g. a 21.1% efficient PSC lost only 3.2% of its initial PCE after 1200 h at MPP and 65°C).\(^{84}\)

The **perovskite layer** is indeed the most challenging one. First, the lead issue must be addressed, even knowing that the lead content is very low. Since removing it from the configuration will seriously compromise the PCE, an encapsulation method has to be carefully developed to avoid leakages, either extracted by rainwater or emitted as gas phase as in the case of a fire. Concerning fire, the laser-assisted glass-encapsulation method will probably withstand the fire high temperatures, even when subjected to the fire high temperatures.\(^{118}\) If the glass is modified to withstand the fire high temperatures without melting, the sublimated lead will react with the glass encapsulation, creating a lead-glass and capturing lead before it leaks. This method will provide good encapsulation and will avoid environmental degrading agents such as oxygen and moisture to reach the perovskite active layers. Regarding the lead leakage extracted by rainwater from a broken panel, lead-absorbing materials\(^{23}\) can be incorporated in the glass covers (top and bottom), and it can even be used together with a self-healing materials\(^{24}\) to decrease even further the lead escape likelihood.

For the perovskite deposition, the most promising scalable methods are blade coating, slot-die and inkjet. Panasonic announced an astonishing PSM with inkjet deposited perovskite, which demonstrates the potential of this technique.\(^{144}\) However, few details were revealed about the perovskite deposition. On the contrary, slot-die coating was reported to prepare a 144 cm\(^2\) PSM.\(^{152}\) This technique can also be used to uniformly deposit the perovskite solution onto the tri-layer porous stack of a monolithic structure.\(^{153}\)

Concerning the perovskite formulation, the most used is the simple MAPbI\(_3\). MA is usually reported in the devices with higher efficiencies, but FA has a higher thermal stability. MA-based cells also degrade significantly when in open circuit. FA-based perovskites spontaneously transit to the 5-phase when exposed to ambient moisture, but if caesium is incorporated that transition is inhibited. Iodine is also the most used anion because it allows obtaining a band gap near to the ideal, but adding or replacing it by bromine increases the long-term stability. Regarding solvents, the widely used DMF is very toxic and must then be avoided for the safety of the staff. On the contrary, the molten salt methylammonium acetate (MAAc) has negligible vapour pressure, and it is non-hazardous and cells prepared using this solvent can reach a PCE of 20% even if deposited under 80% RH.\(^{190}\)

Other compounds that enable the perovskite deposition under high RH are NH\(_4\)Cl, KSCN and NH\(_4\)SNC.

The perovskite formulation used in the 144 cm\(^2\) slot-die-coated PSM was Cs\(_{0.14}\)FA\(_{0.86}\)Pb\(_{1.55}\)Br\(_{0.45}\) with DMSO as main solvent.\(^{152}\) It is not clear if the atmosphere during deposition was inert, but 0.7% in volume of NH\(_4\)Cl can be added to enhance the perovskite crystallization under ambient atmosphere.\(^{192}\) Additionally, a dry-air or nitrogen knife stream could be implemented to enhance forming high-quality perovskite crystals and diminish instant degradation caused by ambient moisture.\(^{185}\) Another suitable alternative is the use of a tri-cation perovskite with low content of MA (Cs\(_{0.05}\)(FA\(_{0.90}\)MA\(_{0.08}\))\(_{0.95}\)Pb(I\(_{0.92}\)Br\(_{0.08}\))\(_3\)) doped with 0.1% oleylamine (OAm)\(^{108}\) and coated with 3.5 nm of a lead sulphate film.\(^{84}\) The long oleylamine chains promote a favourable perovskite grain orientation, while the lead sulphate thin layer (insoluble in water) passivates the undercoordinated surface lead centres that act as defect-nucleating sites, which together boosts the PSC PCE and stability. The lead sulphate layer can be prepared by dipping the perovskite film into 4 mM (C\(_8\)H\(_{17}\)NH\(_3\))\(_2\)SO\(_4\) and (C\(_8\)H\(_7\)NH\(_3\))\(_3\)PO\(_4\) solutions for 20 seconds followed by thermal annealing. The selected solvent in the oleylamine study was DMF/DMSO=4/1. The non-hazardous MAAc is also a good option. Moreover, doping the tri-cation perovskite (Cs\(_{0.15}\)FA\(_{0.84}\)MA\(_{0.41}\))Pb(I\(_{0.92}\)Br\(_{0.08}\))\(_3\) with 0.1% of NaF also enhances the PSC stability by passivating both cation and anion vacancy defects.\(^{104}\)

Concerning the **monolithic structure**, it is perhaps the simplest architecture to fabricate. It does not require a HEL, and the EEL, scaffold and carbon BC can be screen-printed. The perovskite layer can be then deposited by slot-die—it was reported a PSM using a MAPbI\(_3\) perovskite doped with 5-AVAI and using GBL as solvent displaying a PCE of 12.9%.\(^{155}\) However, 5-AVAI-doped MAPbI\(_3\) was not evaluated regarding thermal stability. Instead of 5-AVAI, it could be used 1% ETI—increases both the perovskite thermal stability and moisture resistance.\(^{103}\) However, the monolithic structure requires high-temperature sintering...
steps: 500°C for TiO₂ EEL, 500°C for ZrO₂ scaffold and 400°C for the carbon BC, for 30 min each. After depositing the perovskite, the whole structure should be annealed at 50°C for 4 h. Finally, three PSC designs were defined according to this discussion—Figure 30. Although not being part of the scope of this review, it is also worth mentioning that there is still another possible design for a perovskite-based solar cell, which is the multi-junction (tandem) solar cell. In this structure, two light absorbers with complementary band gap energies are used in the same device, with the purpose of increasing the performance by broadening the absorption wavelength of the device. Given the absorption spectrum of silicon and perovskite, these two materials are often used together to form multi-junction solar cells, being the current record efficiency 29.1%²¹¹,²¹²

8  |  CONCLUSION

The current intensification of environmental ethics has boosted the market of renewable energy. Despite this mind-set change, Lazard’s latest annual Levelized Cost of Energy Analysis concluded that the global levelized cost of energy generation by a photovoltaic utility (≈30 €·MWh⁻¹) is three times lower than the global levelized cost of energy generation by coal (≈92 €·MWh⁻¹).²¹³ Thus, the photovoltaic energy market and the other commodities associated with this type of energy (e.g. batteries for energy storage) will certainly experience a substantial growth in the following years. Actually, the investment on new solar farms is rising every year, and if this trend is maintained, by 2027 photovoltaic power will contribute with ca. 20% of the global energy market.²¹⁴

This increasing interest in the photovoltaic electricity stimulates the growth of other technologies, such as perovskite solar cells. Perovskite is synthesized at room or close to room temperature, unlike silicon which needs several purification processes and synthesis temperatures of ~2000°C. By optimizing the PSC manufacturing procedure in environmental terms, the energy consumption and the emission of greenhouse gases can be significantly mitigated. Additionally, PSCs can have different colours, shapes, levels of transparency and can also be built in flexible substrates, which makes this technology more versatile and aesthetically appealing.

In this work, a thorough review of the state-of-the-art on the present PSC challenges—PCE, costs, stability, up-scaling and environmental impact—is made. Since the range of materials available for assembling a PSC is wide (about 80 were identified in the supporting information), it was identified the ones with a better cost-effectiveness ratio. Strategies to enhance PSC stability are presently the area with probably more publications. It includes doping the perovskite and charge extraction layers, the use of more stable charge extraction layers, adding passivation/protective layers and perovskite crystallization engineering. The most relevant ones were presented and discussed. The reported deposition methods, not only for the perovskite layer but also for the other functional layers, were filtered according to the effectiveness and fabrication process simplicity (atmosphere conditions as well). Strategies to decrease the environmental impact are also presented. Finally, the whole information was holistically analysed, and the most promising works were put together in a final chapter.

The amount of research towards overcoming these PSC challenges is simply huge. New breakthroughs are constantly coming out, making the first commercially available PSC an anticipated event for the coming couple of years. The goal of assemble together these recent advances in this review is to help the research community understanding the stage that the PSCs achieved and what is still needed.

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