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Progress, challenges and perspectives in flexible perovskite solar cells

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1. Structure and optoelectronic properties of perovskite films

1.1 Crystal Structure of Perovskite

The basic structure of any type of perovskite material is shown in Figure S1. The generic formula is ABX₃, where "B" is generally a metallic cation surrounded by anions "X" forming a BX₆ octaedra, creating a three dimensional framework.¹ "A" is another cation, typically bigger than "B", that balances the charges and fills the interstitial sites between the octaedra. For a material to crystallize in a perovskite structure, some constraints on the ratio between the ionic radii of the constituent components exist, in order to fill the lattice and stabilize the structure.² Hundreds of compounds exhibit a perovskite structure, including MgSiO₃ which is the most abundant material on earth.³ Several perovskites are used as functional materials, for instance in piezoelectric or superconductive applications.⁴



Figure S1: Scheme of a typical perovskite crystal structure where A is CH₃NH₃⁺, B is Pb²⁺ and X is I⁻ for one of the typical CH₃NH₃PbI₃ perovskite semiconductors used in solar cells.

It is the class of hybrid metal halide perovskites which is used in PV applications, where A is an organic cation, B is Pb²⁺ and X is a halide anion. It is possible to tune the opto-electrical properties of the material by changing or mixing different halides or organic cations. The most commonly used compound is CH₃NH₃PbI₃. This material has 4 solid phases, and three of them are perovskite called α , β and γ , while δ -phase does not exhibit a perovskite structure.⁵ At high temperatures (above 327 K), CH₃NH₃PbI₃ shows a pseudo-cubical α -phase. If the temperature is cooled under 327 K, the perovskite undergoes a phase transition to the tetragonal β -phase. In both α and β the orientation of methylammonium cations is not defined, and a reorientation of this cation under electrical field or incident light might explain the ferroelectric response observed in this material. If the temperature is lower than 162 K, the perovskite displays an orthorhombic γ -phase. The transition to the δ -phase can be observed when a solvent is present in the system. X-ray

diffraction (XRD) can be helpful in identifying the phase of the material (cubic or tetragonal) and the preferred growth orientation.⁶ If the iodine is partially substituted with a smaller cation such as Br, the temperature of phase transition from β to α -phase gradually increases, and it is possible (at 13% Br content with respect to the total halogen content) to stabilize the cubic phase at room temperature.⁷

1.2 Optoelectronic Properties of Perovskite

The great interest in this class of perovskite lies in the remarkable opto-electronic properties of this material which can also be solution-processed. CH₃NH₃PbI₃ is an intrinsic semiconductor with a band gap of 1.55 eV.⁸ Thus the absorption onset is close to 800 nm, with strong absorption in the whole of the visible spectrum. Figure S2 shows that the absorption coefficient of CH₃NH₃PbI₃ is much greater than that of crystalline silicon (permitting one to use much thinner layers for PV applications) and equal or higher with respect to most of the materials used in the thin-film technologies (except CIS an CIGS).¹



Figure S2. Comparison of absorption coefficients as a function of wavelength of many common materials used in photovoltaic cells.¹ Adapted by permission from Macmillan Publishers Ltd: Nature photonics 8.7 (2014): 506-514., ¹"The emergence of perovskite solar cells." copyright 2014

A perovskite layer of ~300 nm is usually considered adequate to absorb the light in a solar cell, especially if a back-reflecting top electrode is used.⁹ DFT simulations indeed show that CH₃NH₃PbI₃ possesses a direct bang gap.¹⁰ Interestingly, a simulation of the possible crystal defects and the trap levels arising from these show that most of these traps lie outside the band gap or very close to the valence or conduction band.¹¹ Thus, especially for recombination, the effect of such defects is not so critical on the device performance. This might explain how solution processed PSC can exhibit a very high open circuit voltage, of up to 1.1 V or more, with a very small voltage loss compared to other systems, with respect to the value of the band gap of the semiconductor.¹

The photophysics of this material is rather complicated and the understanding of these properties goes behond the purpose of this review.¹² Nevertheless is already possible to point out that most excitations in this semiconductor lead to free-charges since the exciton binding energy is comparable to the thermal energy k_BT at room temperature.¹³

The diffusion length, L_d, is the length electrons and holes are able to freely diffuse in a given material before recombining, and this value is relatively high for this material. For collecting charge efficiently, it is important that the thickness of the photoactive layer does not exceed the diffusion length. For Cl-containing perovskite the diffusion length can be as high as 1.9 µm for electrons (~1.2 µm for holes) as measured with Electron Beam Induced Current (EBIC) analysis.¹⁴ The same report showed that CH₃NH₃PbI_{3-x}Cl_x behaves as an intrinsic semiconductor whilst CH₃NH₃PbI₃ exhibits a slightly p-type behaviour.¹⁴ The intrinsic nature is confirmed also by the carrier density of 10⁹ cm⁻³, similar to intrinsic silicon, while the electron mobility (for CH₃NH₃PbI₃ is ~66 cm² V⁻¹s⁻¹) is lower.¹⁵ The properties of the thin-film are usually different from single crystal materials, due to the reduced crystallinity and to the presence of grain boundaries. Indeed, the longest diffusion length (exceeding 3 mm) was observed in a CH₃NH₃PbI₃ single-crystal under weak light illumination, where a hole diffusion length of $\sim 175 \,\mu m$ was measured under one sun illumination (electron and hole mobilities calculated using Hall effect measurements were 105±35 and 24.8±4.1 cm²V⁻¹s⁻¹ respectively), confirming the high potential of this material for photovoltaic applications.¹⁶

1.3 Chemical tailoring of bandgap

It is possible to tune the band gap of the material by changing its chemical composition, e.g. introducing some Br.⁷ In Figure S3 the absorbance and the band gap of $CH_3NH_3PbI_{3-x}Br_x$ is shown. By adding Br, a monotonic increase of the band gap is observed. Furthermore, the addition of small amount of Br improves the light absorption at wavelengths close to the absorption onset, improving the light harvesting in the red part of the visible spectrum. Indeed, this chemical modification is often used for highly efficient PSC.^{17, 18} Finally, as a result of lattice distortion, CH₃NH₃PbI_{3-x}Br_x seems to be less sensitive to moisture.⁷



Figure S3. Optical properties of CH₃NH₃PbI_{3-x}Br_x as a function of Bromine content x a) absorbance onset b) picture of a thin-film of CH₃NH₃PbI_{3-x}Br_x on glass c) gradual evolution of the band gap.⁷ Reprinted from Nano letters 13.4 (2013): 1764-1769. "Chemical management for colorful, efficient, and stable inorganic–organic hybrid nanostructured solar cells.". Copyright 2013 American Chemical Society

Whereas the addition of Br and its effects on the material properties of the resulting perovskite are well-explained, the role of Cl anions is not yet clear.¹⁹⁻²² Indeed, Cl is usually added using a different perovskite synthesis, by means of a non-stoichiometric mixture of PbCl₂ and CH₃NH₃I, and the product is called CH₃NH₃PbI_{3-x}Cl_x since the amount of Cl is unknown. Since this synthetic route is different from the usual one, it is hard to distinguish between the role of Cl

in the crystallization process and its stoichiometry in the perovskite material itself. The presence of Cl in the perovskite film after the annealing process which is used to convert the precursors into a semiconducting film is not evidenced. Nevertheless, Cl addition is often reported to increase the diffusion length of both electron and holes, and recent studies correlate this effect both to the different crystallization path, and to the actual doping of CH₃NH₃PbI₃.^{21, 22} It has been also suggested that the formulation containing Cl might be not the best if one wants to build PSCs incorporating a mesoporous layer.²³ Finally, more exotic substituents, for instance a SCN group, can substitute the I anions, giving a moisture resilient device with decent efficiency.²⁴

The organic cation is another element that can be changed to tune the properties of the perovskite crystal. A well- known modification uses formamidinium iodide, a slightly bigger cation with respect to methylammonium.²⁵ The resulting perovskite is a polymorphic material, and only the high temperature phase (above 160°C) would show interesting photovoltaic properties. Unfortunately this phase is not highly stable at room temperature, especially in moist environment.¹⁷ The band gap of this perovskite is slightly lower with respect to the methylammonium based one, improving light harvesting in the infrared region. Thus there have been efforts in including this material in solar cells. In fact, the phase instability can be overcome using 15% of methylammonium or caesium anions to stabilize the high temperature phase.^{17,26, 27} This kind of mixture ensured the highest reported efficiencies for PSCs which to date are between 20% and 22% on glass²⁸⁻³¹.

Bigger cations may result in the breakage of the three-dimensional lead iodide framework, creating a layered structure, not particularly interesting for PV applications, while small inorganic cations such as Cs can also be used as dopant.^{32, 33} Obviously the main component that has been touted for change in CH₃NH₃PbI₃ has been the Pb cation, due to its possible toxicity (see following

LCA analysis, section 13.2). The use of Sn had been already meticulously studied in the early 90's and initial promising efficiencies of up to 6% have been recently reported.^{34, 35} However the reduced diffusion length (30 nm) and the very limited stability of tin-based perovskite if not solved can limit interest in this type of configuration.³⁵ Moreover, the amount of Pb in PSC is smaller than the amount of Cd in CdTe technology, so without a careful analysis of the life cycle of PSC from production to recycling, it is hard to quantify the real danger related to the use of lead.^{1, 36, 37}

2 Working mechanism and device architectures of perovskite solar cells

In a PSC, the perovskite layer is sandwiched between a p-type layer, also called HTM (Hole Transport Material), and a n-type layer, also called ETL (Electron Transport Layer), creating a p-i-n configuration. An example of the set of materials used as ETLs and HTMs is shown in Figure S4 (left). Note, for example that the electron affinity of the ETL must be slightly larger than that of the perovskite absorber in order to permit an energetically-efficient extraction of electrons.

The working mechanism of PSC resembles to a certain extent that of a p-i-n heterojunction, with the intrinsic perovskite sandwiched between two extraction layers with some variation depending on the architecture, as will be discussed later on.¹⁴ Differently from inorganic homojunction silicon p-i-n diodes, the n and p are made of different materials some of which are also in an undoped form. The bottom layer can be either the ETL or the HTM, but the processes involved are the same and are schematized in Figure S4 (right).



Figure S4. Left) Energy levels for different materials acting as ETLs (left), absorbers (middle) and HTMs (right) in perovskite solar cells.⁸ Reprinted from Materials Today, 17-1, Pablo P. Boix,Kazuteru Nonomura,Nripan Mathews,Subodh G. Mhaisalkar, Current progress and future perspectives for organic/inorganic perovskite solar cells, 8, Copyright 2014, with permission from Elsevier. (right) working mechanisms (green arrows) and recombination paths (red arrows) in a perovskite solar cell. TiO₂ can be replaced with other ETLs.¹ Adapted by permission from Macmillan Publishers Ltd: Nature photonics 8.7 (2014): 506-514."The emergence of perovskite solar cells." copyright 2014

Light promotes electrons from the perovskite valence band to the conduction band (1). The weakly-bound exciton, splits into free charges, and thus PSCs are better represented by a free carrier model.³⁸ The electrons and holes can thus drift-diffuse towards the selective contacts and the charges are finally extracted (2 and 3).¹ Charge generation and collection rates are competing with those of recombination. Electron-hole recombination can occur in the perovskite layer itself (4), between electrons in the ETL and holes in the perovskite (5), between electrons in perovskite and holes in the HTM (6), and between electrons in the ETL and holes in the HTM (7), especially if these come in contact due to non-uniform perovskite films. To improve the efficiency of a PSC, one has to improve light harvesting and charge extraction while also suppressing as much as possible the recombination processes. In this section we analyse the effect of device architecture on the working mechanism of PSC.

An important aspect that needs to be introduced is the hysteresis phenomenon that occurs while measuring PV performance of a PSC.³⁹ Indeed measuring the IV curve of a PSC in both

forward and reverse direction typically results in a different IV curve. The origin of this effect is still under debate, but iodine migration due to polarization is considered to be one of the main causes.⁴⁰ By applying an electric field to the perovskite film it is possible to generate a built-in potential, due to the migration of iodine ions, which temporarily improves charge extraction. This is a transitory effect that can led to overestimation (reverse scan) or underestimation (forward scan) of the PCE, making the IV characterization of PSC not straightforward. Indeed, arguably the best way to measure a PSC, is the quasi steady state measurement in which the current is measured with the cells polarized at their maximum power point.⁴¹ Unfortunately, most of the papers published from 2013 to 2015 do not present this kind of analysis, so that researchers should carefully assess the results presented. For example, a PSC without a compact ETL may show high PCE with a fast reverse scan, while the steady state PCE is close to zero.^{42,43} We also suggest that PSCs that show huge hysteresis may be considered not stable and deployable, since usually the best performing PSCs present a nearly hysteresis-free behavior.⁴⁴

PSCs have been fabricated in a variety of different configurations as a result of the versatility of the perovskite and extraction layer combinations. The latter had often been previously developed for second and other types of third generation solar cells (e.g. OPV and DSCs).⁸ To classify the different architectures used in PSCs, two main classifications are analysed here. First, PSCs can be divided in mesostructured and planar. In the former, at least one among the ETL or HTM stack components is fashioned into a mesoporous layer, while in the latter both ETL and HTM can be considered planar/flat films (see Figure S5).



Figure S5. (Top panel) Scheme of a mesoporous (a) and planar (b) perovskite solar cell.⁸ Reprinted from Materials Today, 17-1, Pablo P. Boix,Kazuteru Nonomura,Nripan Mathews,Subodh G. Mhaisalkar, Current progress and future perspectives for organic/inorganic perovskite solar cells, 8, Copyright 2014, with permission from Elsevier. (below, left) cross-sectional SEM picture of a n-i-p mesoporous PSC using TiO₂ as ETL and polyarylamide (PTAA) as HTM of the type shown in scheme (a).⁴⁴ Adapted by permission from Macmillan Publishers Ltd: Nature material 13.9 (2014) ⁴⁴ "Solvent engineering for high-performance inorganic–organic hybrid perovskite solar cells." copyright 2014. From Science, 345-6194, ⁴⁵ (below, right) scheme of the "triple-layer" perovskite structure, where the perovskite is infiltrated in a mesoporous TiO₂- insulator-Carbon stack. ⁴⁵ For all architectures only the n-i-p structure is shown. In the p-i-n structure the position of the ETL and HTM are switched. A hole-conductor–free, fully printable mesoscopic perovskite solar cell with high stability. Reprinted with permission from AAAS."

Even if the top extraction layer is considered to be "planar", there is evidence that it can infiltrate into the perovskite structure, especially at its grain boundaries.^{46, 47} Using materials like Phenyl-C₆₁-butyric acid methyl ester (PCBM), which are able to passivate some of the perovskite defects, enables one to achieve improved performance.⁴⁸ Moreover, the additives used in the HTM are not only dopants of the HTM itself, but will also affect the perovskite layer.⁴⁹

A second classification can be made on the basis of the nature of the bottom layer on which the perovskite is deposited: historically, the architecture is defined direct if the bottom layer is the ETL (n-i-p) or inverted in the other case (p-i-n). Four main classes of PSCs have been defined in this way: planar n-i-p PSC, mesoporous n-i-p PSC, planar inverted (p-i-n) PSC and mesoporous inverted (p-i-n) PSC. Additional configurations having peculiar characteristics will be discussed in the section 3.3.

2.1 Conventional architecture of PSCs (n-i-p)

Representing both the first to be made and the most efficient solid state perovskite solar cells (PSC) to date with efficiencies of up to 20-21% is that based on a n-i-p mesostructured architecture device similar to a solid state DSC (Figure S5a).^{28, 29, 31} The TCO (Transparent Conductive Oxide)-coated glass substrates are covered with a double layer (compact + mesoporous) of TiO₂, the latter infiltrated with perovskite. An additional capping layer of perovskite over the mesoporous TiO₂ can be used to prevent recombination between the ETL and the HTM. The compact TiO₂ is needed to inhibit charge recombination between the TCO and the perovskite. In the best-performing cells, typical thicknesses of the constituent layers are the following: 50 nm for the compact layer, ~200 nm for the mesoporous layer, 200 –300 nm for the perovskite capping layer, while the thickness of the HTM depends on the material used (50 nm for PTAA and 200 nm for Spiro-O-MeTAD).^{29, 50} The mesoporous layer plays two roles: enhancing the electron extraction, and enabling a more homogenous polycrystalline growth of the perovskite. The fast electron extraction can also be seen in the reduced hysteresis reported for this architecture.⁴⁴ The drawback of this design consists mainly in the high temperature usually

required for producing an effective TiO_2 layer, but other low temperature techniques applicable to flexible substrates have been developed.⁵¹⁻⁵⁵

The mesoporous scaffold may be composed of Al_2O_3 nanoparticles where, unlike the TiO₂, electron injection is energetically not possible.⁵⁶ This kind of approach has been investigated especially in cells in combination with $CH_3NH_3PbI_{3-x}Cl_x$ perovskite with which better results have been produced.⁵⁷ The role of the insulating Al_2O_3 is not completely clear, but the scaffold definitely modifies the substrate enabling an easier growth of a homogenous perovskite layer, even without a high temperature sintering step.⁵⁸

The other n-i-p structure is that of the planar cell which appears potentially easier to fabricate. TiO₂ is also used as the compact ETL, but here it needs to fulfil two roles efficiently: electron injection and hole blocking. While the latter is easily ensured, the former not as often reproducibly which can result in poor charge extraction and indeed strong hysteresis in the J-V curves.⁵⁹ Efforts have been put in optimizing the interfaces at the contacts to improve electron injection.⁶⁰ For instance the TiO₂ can be substituted with ZnO⁶¹ or SnO₂^{62, 63} which offer many fold higher electron mobility,^{64, 65} obtaining better performance and reduced hysteresis. Another interesting development for ETL engineering is the use of fullerene compounds to enhance the electron extraction.⁶⁶ Fullerenes can create hysteresis-free devices in the p-i-n structure, thanks to the very high electron affinity and its ability to intercalate the perovskite grains.⁴⁸ On the other hand, the solvent used for perovskite deposition can dissolve the fullerene layer, so for the n-i-p structure, thermal evaporation of the perovskite is required to avoid damage to the fullerene-based ETL.⁶⁶ A way to overcome this issue is to blend the PCBM within the perovskite itself, creating a network of PCBM that surrounds the grain boundaries, helping both charge extraction and defect passivation leading to hysteresis-free devices.⁶⁷

2.2 p-i-n architecture of PSCs

The most common planar architecture is that where the hole extraction layer is on the conducting substrate (sometimes termed as "inverted"). In the most common stack, the perovskite sandwiched between а poly(3,4-ethylenedioxythiophene)-poly(styrene is sulfonate) (PEDOT:PSS) HTM and a PCBM ETL.⁶⁸ This architecture benefits from efficient charge extraction arising at these materials that had been extensively developed from organic semiconductor technologies with PEDOT:PSS known to have a high work function with also beneficial effects on the built-in potential⁶⁹ and PCBM possessing both high electron affinity and mobility⁷⁰. PEDOT:PSS/perovskite/PCBM cells have resulted in hysteresis-free devices, with PCEs higher than 17% reported various times.^{46, 68, 71} One main drawback of this type of planar device lies in the use of PEDOT:PSS, a material known to be unstable over long term timescales, especially if not properly encapsulated.⁷² Thus several investigations have been carried out to substitute PEDOT:PSS with other HTMs such as Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA), NiO, graphene oxide or polythiophenes.^{71, 73-75} On the matter of stability, further comparative investigations of these scaffoldless devices with those that do present a scaffold would be useful to determine the role of the scaffold and processing conditions on the lifetime of flexible perovksite solar cells.76-78

The ETL interface has been carefully investigated too, and several interfacial layers can be used on top of PCBM, such as TiO₂, C_{60} or bathocuproine (BCP). ^{95 68, 79, 80} An alternative to the planar concept is the "mesostructured" p-i-n design that incorporates a p-type NiO mesoporous layer and a PCBM top ETL with efficiencies of 11.6%.⁸¹

2.3 Other device architectures for PSCs

There are others device stacks that do not fit easily in the above classifications: devices without HTM, where the p-type electrode also acts as HTM, devices with a non-injecting mesoporous layer and devices with a fully mesoporous architecture. In the HTM-free design, the top hole-extracting contact, consisting in a stable material with appropriate energy levels such as gold or carbon, is typically directly deposited on top of the perovskite.^{82,83} The simplicity and the exclusion of often the most expensive layer are the main advantages of the HTM-free design, although higher recombination rates due to the absence of an electron blocking interlayer may lead to lower open circuit voltages and PCEs.⁸⁴

Finally, a device architecture that recalls the monolithic DSC structure was successfully implemented in PSCs (Figure S5, below right).⁴⁵ A triple layer of mesoporous TiO₂, mesoporous ZrO₂ and mesoporous carbon on top of a compact layer of TiO₂ was printed over a conducting substrate. The perovskite was finally infiltrated trough the carbon electrode to fill the structure. This architecture has shown remarkable stability over 1000 hours of light soaking test without any encapsulation.^{45, 85} The stability, printability and low cost of this structure make it a promising approach for up-scaling perovskite solar cells. Even if carbon can work as a selective p-contact, an additional mesoporous nickel oxide interlayer can be printed in between ZrO₂ and carbon to improve hole injection, resulting in a PCE of 14.9%.⁸⁶ A similar study uses a mesoporous metallic nickel top electrode instead of carbon, obtaining a PCE of 13.6%. An additional feature of the latter device was the possibility of washing the degraded perovskite and filling the structure with a fresh solution, obtaining a PCE similar to the original one.⁸⁷

3 Deposition and Synthesis methods of perovskite thin films

The synthesis of the hybrid metal halide thin-film is generally achieved by reacting a lead halide salt with a methylammonium halide salt. The stoichiometric reaction is the following:

$CH_3NH_3I + PbI_2 \rightarrow CH_3NH_3PbI_3$

There are two main approaches to perform and control this reaction: single-step and double-step (also called sequential deposition method).⁸⁸ Although methods such as vapour-assisted vacuum deposition⁸⁹⁻⁹³ and thermal evaporation deposition⁹⁴ of perovskite are often classified as separate methods, one may also include them as a modification to sequential or single step method. Solution processing is most widely used but, but thermal evaporation of the precursors or of the whole perovskite has also been demonstrated.⁹⁵

3.1 Single step deposition of perovskite precursors

In the single step reaction, the two precursors are dissolved in the same solution. The solvent has to dissolve both the precursors and inhibit precipitation of perovskite. Thus a limited set of solvents has been used so far, and most of the papers employ N,N-Dimethylformamide (DMF), Dimethyl sulfoxide (DMSO) or γ -Butyrolactone (GBL).⁹⁶ The perovskite crystallize directly on the substrate and a controlled nucleation and growth of the crystals is crucial for obtaining smooth efficient films. Indeed the deposition technique, as well as the substrate itself, will have a strong impact on the final film morphology. ⁹⁷

This precursor solution is usually deposited on the substrate by spin coating and after a rapid annealing step (typically less than 10 minutes at 100°C) the perovskite layer is formed. Spin coating ensures a very fast drying of the solvent, helping to promote crystal nucleation and a more homogenous film formation.⁹⁸ However even using the solvent with the lowest boiling point (i.e.

DMF from the group mentioned above) the film obtained with this method is still not homogenous, as shown in Figure S6 (top left), especially on planar substrates. ⁹⁹



Figure S6. SEM image of: (top left) single-step perovskite film using only DMF as solvent, without other additives; ⁹⁹ Adapted by permission from Macmillan Publishers Ltd: Scientific Reports 4 (2014): ⁹⁹ " Planar heterojunction perovskite solar cells with superior reproducibility" copyright 2014 (top right) a perovskite film obtained with a solvent dripping method; ⁴⁴ Adapted by permission from Macmillan Publishers Ltd: Nature material 13-9 (2014)⁴⁴ "Solvent engineering for high-performance inorganic–organic hybrid perovskite solar cells." copyright 2014 (bottom left) perovskite layer obtained by dipping PbI₂ in a CH₃NH₃I solution; ¹⁰⁰ Adapted by permission from Macmillan Publishers Ltd: Nature photonics 8-2 (2013) ¹⁰⁰ "Perovskite solar cells with a planar heterojunction structure prepared using room-temperature solution processing techniques." copyright 2013. (bottom right) perovskite obtained with a CH₃NH₃I vapour.¹⁰¹ Adapted with permission from Journal of the American Chemical Society 136-2 , 622-625.¹⁰¹ "Planar Heterojunction Perovskite Solar Cells via Vapor-Assisted Solution Process" Copyright 2014 American Chemical Society

Several improvements have been developed in order to get a homogenous film: use of additives such as HI or CH₃NH₃Cl, addition of very high boiling point solvents, solvent dripping method or PbCl₂ method.^{44, 57, 99, 102, 103} The solvent dripping technique forms PbI₂-DMSO-CH₃NH₃I complex precipitates on the substrate by dropping an antisolvent while spinning a solution of the two precursors. The complex is later transformed to perovskite by fast annealing (from 1 to 10 minutes at 100°C), leading to highly efficient solar cells thanks to the closely packed grain morphology of the film (Figure S6, top right). ^{44, 50}

The PbCl₂ method is one of the most-used synthetic processes, and provides high efficiencies especially in planar devices.^{23, 57, 60} In this process, the precursor solution is made by mixing PbCl₂ and CH₃NH₃I in a 1 to 3 molar ratio, and the perovskite obtained is usually named CH₃NH₃PbI_{3-x}Cl_x even if the name might be misleading. Indeed, there is no strong evidence that the Cl is always present in the final film and it is unlikely that Cl is substituting I atoms due to the very different size. Therefore, the role of Cl-substitution is still under debate. This ink is coated, dried and transformed to perovskite by thermal annealing. The proposed perovskite formation reaction is the following:¹⁰⁴

$$3 \text{ CH}_3\text{NH}_3\text{I} + \text{PbCl}_2 \rightarrow \text{CH}_3\text{NH}_3\text{PbI}_3 + 2 \text{ CH}_3\text{NH}_3\text{Cl}$$

Some deviation from this clean reaction is expected to allow small amounts of Cl incorporation in the final film. Furthermore, the methylammonium chloride may be split in methylamine and HCl. The annealing time is much longer that that used in the PbI₂ route, up to two hours, since large excesses of methylammonium and Cl inhibit the fast-crystallization observed in the stoichiometric reaction.¹⁰⁵ The samples are first dried and then annealed. Crystallization does not start at temperatures below 60° C.^{104, 106} The separation of drying and annealing steps makes it easier to up-scale the technology with different coating techniques (e.g. blade coating), where it is hard to

obtain fast drying of the films which instead happens naturally with spin coating.⁷⁹ It is possible to accelerate the conversion rate by using lead acetate instead of lead chloride, taking advantage of the faster evaporation of methylammonium acetate with respect to methylammonium chloride.¹⁰⁵ Use of PbCl₂ led to remarkable efficiencies for planar devices (up to 19.3%), whilst not as high for mesoporous cells.^{23, 60} The perovskite layer obtained with this method is generally not as smooth as the one produced with solvent dripping or other high efficiency synthesis methods.

3.2 Double step or sequential deposition of perovskite precursors

A different approach consists in synthetizing the perovskite with two different coating steps. The first is the coating of the substrate with the lead precursor (usually PbI₂), by either solution processing or thermal evaporation which is then converted to perovskite by adding the organic salt, usually by dipping in a CH₃NH₃I solution in isopropanol.^{88, 107} The conversion takes from a few seconds to several minutes, depending on the PbI₂ morphology/porosity.⁹⁸

A drawback of this technique is that the conversion might not be complete if the PbI₂ is too compact or the dipping time is too short, affecting both efficiency and stability.¹⁰⁸ For this reason and for the sake of easier processing, the morphology of the PbI₂ layer has to be controlled to allow an easier conversion.¹⁰⁹ Furthermore, alternative conversion procedures have been investigated. Use of CH₃NH₃I vapour, printing of CH₃NH₃I solution on top of the PbI₂ layer (also called interdiffusion method) and heat-pressure contact with a CH₃NH₃I film are possible strategies.¹⁰¹ ^{110, 111} These methods can ensure also better perovskite morphology by producing a smoother layer as shown in Figure S6 (bottom images c& d).

Chemical tailoring of CH₃NH₃PbI₃ is possible also in the double step synthesis. CH₃NH₃Cl can be used both as a morphology controller, and as a dopant to increase device performance.^{22, 112} Finally, adduct chemistry and use of formamidinium iodide, have represented a winning combination also in the double step route.²⁹ The PbI₂ layer was substituted by a PbI₂-DMSO mixture, and a formamidinium iodide solution was spin coated on top. The organic salt and DMSO underwent a intramolecular exchange, and a high quality perovskite film was produced leading to the first reported efficiency above 20%.²⁹

The double step gives more freedom in the choice of solvents. The second step is usually carried out in a safe solvent (isopropanol), but also solvent-free techniques can be used.¹⁰¹ Thus, by finding a green solvent for PbI₂, it will be easier to develop an environmentally friendly process for perovskite coating. Moreover, PbI₂ can be substituted with other salts with higher solubility (e.g. lead nitrate is soluble in water).¹¹³ From an industrial perspective, the need for a double step synthesis makes manufacturing more expensive. However, the fast annealing time allows one to downscale the furnaces and reduce the energy cost, making the double step a valuable approach.^{114, 115}



Top Assignee(s)



Figure SI 7: Top assignees for (a) *f*-PSCs and (b) *LT*-PSCs.

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