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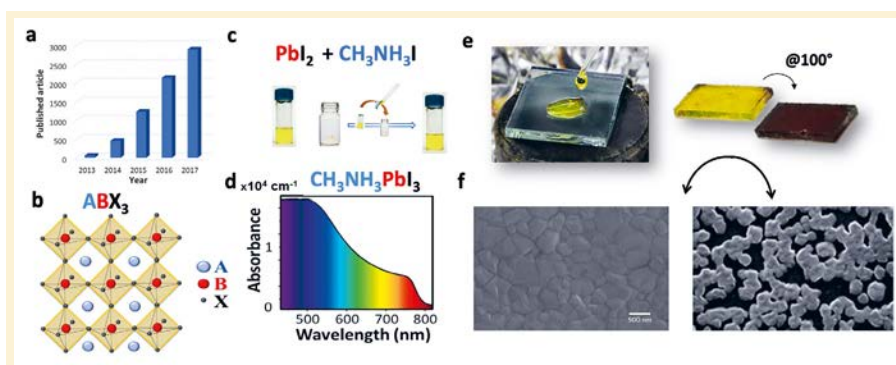


Figure 2. (a) Graph representing the evolution of number of publications related to HP in the last decade. (b) Structure of the 3D HP. (c,e,f) Representation of solution-based deposition process starting from precursors in solution. (f), in particular, represents two possible different morphology which can result from solution process: either a uniform optimized film or a non-uniform film with many cracks and pinholes. Two-years of intense investigation (between 2012 and 2014) lead to the solutions for getting reproducible and uniform perovskite thin films. (d) Absorption spectrum of the MAPbI₃, showing the panchromatic response [1-3].

as potential semiconductors, superconductors and for their optoelectronic and magnetic properties, HP demonstrated to be efficient light antennas and charge transporters – ideal properties for capturing solar power [3]. Solar cells with a HP as the PV-active material, prepared by low-temperature solution-based methods, achieved over 23% certified efficiency after just 10 years of research from a starting efficiency of ~4% (Fig. 1c) [3]. To put this in perspective, the best single-junction inorganic laboratory cell (GaAs) has reached ~29% efficiency after nearly 60 years of research, having started at 4% in 1956. We are now just entered in 2019 the “decade” of perovskite research, in which HP solar cells (HPSCs), have demonstrated impressive performances posing a remarkable challenge to thin film and multi-crystalline silicon PVs (see extract from NREL chart in Fig. 1c). However, for practical application, PV technologies need to be more than efficient – they also need to be stable and scalable, which are the real challenges for the next generation of perovskites solar cells. Stability, in terms of solar cell lifetime, is utmost to address. In addition, HPs present the serious drawback related to the presence of toxic materials, *i.e.* lead [3], with the associated health and environment concerns.

Hybrid halide perovskites materials and solar cells

3D halide perovskites: structure and chemical composition

HP are considered one of the most attractive research topic of our time, as clear from the rapid increase in the amount of publication per year reported (see Fig. 2a). The 3D HPs, such as CH₃NH₃PbI₃, consist of a 3D organic-inorganic crystalline network organized in an ABX₃ structure (see Fig. 2b). A is a small organic cation (e.g. MA = CH₃NH₃⁺), B a metal cation (e.g. Pb²⁺, Sn²⁺), and X a halide anion (e.g. Br, I) [1-3]. The size of the A cations must be small enough to fit within the octahedral unit (Fig. 2b), keeping the integrity of the 3D perovskite structure. The so-called *Goldschmidt tolerance factor* (*t*) sets an empirical limit for it. For the case of CH₃NH₃PbI₃ it reads as: $t = (r_A + r_I) / (\sqrt{2} (r_{Pb} + r_I))$, with $r_{A, I}$ the ionic radii of the A cation and the halide, respectively. The optimal values for the cubic perovskite structure are $0.8 < t < 1$ [1-3]. Considering $t = 1$ as a limit, the maximum *RA* is 2.6 Å (with $R_{Pb} = 1.19$ and $R_I = 2.2$ Å). However, although this represents a *useful rule of thumb* for the screening of new organic cations, the inorganic lattice can



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accommodate even slightly larger organic cations, as for the case of formamidinium (FA = $\text{CH}(\text{NH}_2)_2$) or guanidinium (Gua = $\text{C}(\text{NH}_2)^+$) [1-3]. Compositional engineering has been as one of the keys to improve the structural stability, device stability, and device performance by introducing multiple cations or halides in the perovskite structure. The great advantage of this class of materials, as mentioned above, relies in the easy of deposition methods, adaptable for flexible and large area substrates. For instance, MAPbI_3 can be deposited from solutions. If, at one side, these methods are easy and inexpensive, on the other side, they require the establishment of a precise deposition steps protocol and parameters to obtain, even from solution, high quality crystalline films with large grains and reduced grain boundaries, as shown by the scanning electron microscope images in *Figure 2f*. Not optimal annealing leads for instance to incomplete coverage and not ideal morphology, as shown in *Figure 2f*.

Optoelectronic properties

HPs combine unique electrical and optical properties: high absorption coefficient (that reduces by 10^3 times the optimal device thickness with respect to Si), see *Figure 2d*. In addition, they are characterized by direct photo-generation of free carriers (ionized excitons at room

temperature with low exciton binding energy) [3], efficient charge transport and long carrier diffusion lengths, efficient charge transport and wide band gap tunability, achieved by the manipulation of the A cation or the X halide, as shown in *Figure 3a*. Another striking attribute of these materials is their low non-radiative recombination rates compared to other thin-film polycrystalline semiconductors [3]. These materials show an incredible “defect tolerance”, with low trap density. This property manifests in their high open-circuit voltage (V_{OC}) exceeding 1 V [3]. This places the HP technology in fourth place out of all solar technologies, behind GaAs, crystalline Si and CIGS. Remarkably, the fundamental losses of this new technology are already lower than CdTe, which is the technology of choice for the world’s largest solar company.

Device architectures and efficiency

The unprecedented rate of increase in PV efficiency of HP cells has benefited greatly from earlier research in other classes of PVs. Specifically, the architectures used today draw from dye-sensitized, organic and thin-film polycrystalline compound semiconductor devices, almost without any need to adapt the original architectures to the new

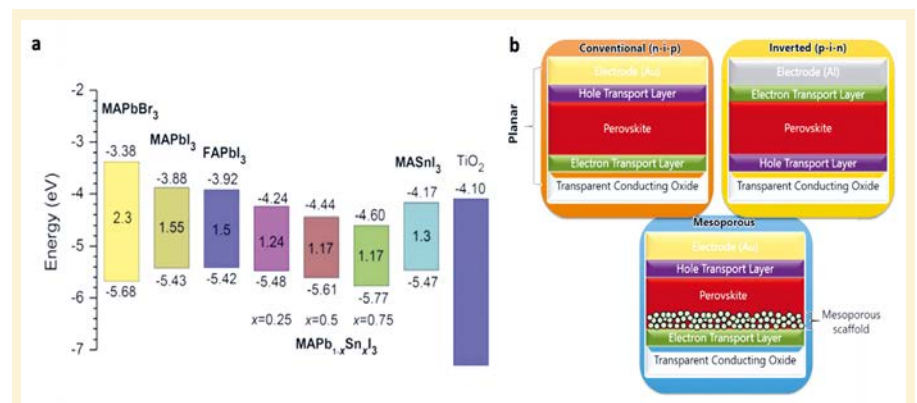


Figure 3. (a) Sketch of energy level for MAPbBr_3 , MAPbI_3 , FAPbI_3 , $\text{MAPb}_{1-x}\text{Sn}_x\text{I}_3$, MASnI_3 and TiO_2 ([1], reprinted with permission from Elsevier). (b) Commonly studied perovskite cell structures in literature: regular (n-i-p) planar, inverted (p-i-n) and regular (n-i-p) mesoporous cell [1-3].

material [1-3]. The solar cell consists of a multi-layered structure (Fig. 3b) where the perovskite is deposited in between an electron transport layer (ETL), and a hole transporting material (HTM). More in details, to sum up, three are the main device architectures, as shown in Figure 3b: mesoporous n-i-p, planar n-i-p and planar p-i-n. A typical mesoporous HPSC comprises an ETL scaffold with nanoscale pores. A perovskite absorber layer covers the scaffold, forming a compact capping layer and also penetrating into the scaffold, leading to an inter-mixed layer. The planar p-i-n architecture is generally referred to as an inverted structure because the carrier extraction layers are inverted with respect to the n-i-p structure. Devices with a p-i-n architecture are often constructed with a planar structure with a compact HTL. As shown from the statistical analysis in Figure 4 and reported in [4], the mesoporous configuration has been the one mostly adopted and the one responsible for the record efficiency. However, in the last year, also the planar configuration made enormous steps forward. Figure 4 depicts the performance of common cell structures through the years in terms of average efficiency as found in literature [4].

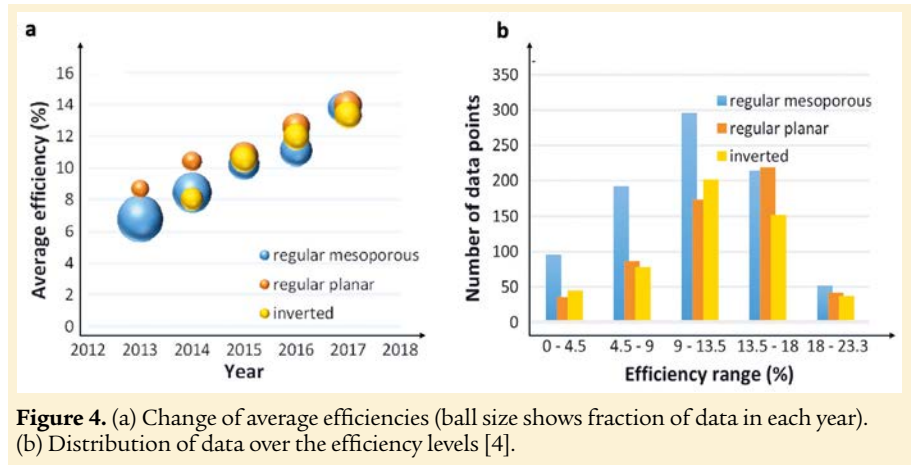


Figure 4. (a) Change of average efficiencies (ball size shows fraction of data in each year). (b) Distribution of data over the efficiency levels [4].

The actual challenge: stability & toxicity

State of the art on material and device stability

Despite the full potential of this technology and the big excitement that came along, a big barrier hampers their commercialization: the poor device stability under operative conditions (HPSCs degrade in ambient air) [3, 5]. For instance, MA-based hybrid perovskite which has been the pioneer and state-of-the-art performances for this class of materials suffers from inherently high instability (i.e. MAPbX₃ decomposes to gaseous methylamine and hydrogen iodide) and susceptible to degradation by heat or moisture [5].

In presence of water they react breaking the 3D crystal structure and then undergoes irreversible decomposition back into the precursors such as PbI₂ [5]. MAPbI₃, for instance, starts to decompose at a humidity of 55%, inducing a remarkable bleach of the color that changes from dark brown to yellow due to conversion into PbI₂ (Fig. 3b). Phenomena such as light induced ion movement, “photo-instability”, or structural deformations not only disturb the material stability, but also alter the device behavior, contributing to the anomalous hysteresis observed in the device current-voltage characteristics that has not yet been clearly understood [3-5]. Despite the urgency, only in the last couple of years research attention has been devoted to

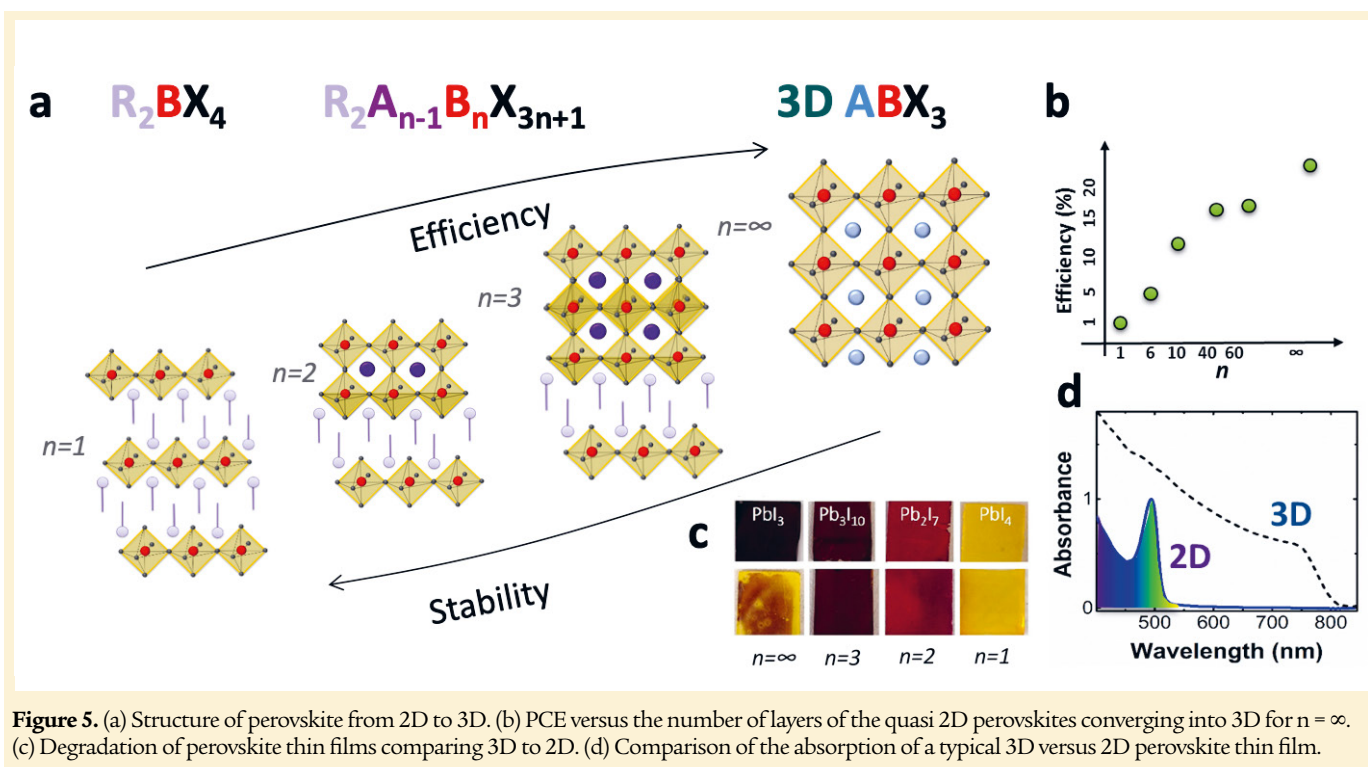
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this issue. On the other side, from the device perspective, each interface and contact layer of the device stack have a key role in determining the overall stability.

Layered perovskite: a solution towards stability

Recently, dimensionality tuning of the perovskite has attracted many attentions in this field. Compared to 3D perovskites, low-dimensional (2D) perovskites exhibit superior stability against the moisture because of the hydrophobic properties of the R cation [ref]. 2D perovskites arrange to *Ruddlesden-Popper* structure with a general formula of $R_2A_{n-1}B_nX_{3n+1}$, where R is a large organic cation (for example, aliphatic or aromatic alkylammonium) which functions as a spacer between the inorganic sheet and n determines the number of inorganic sheets that is being held together [5].

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This structure, shown in *Figure 5a*, makes 2D perovskite very tunable by controlling the cations.

For instance, by controlling A/R ratio, the n value could be adjusted from $n = 1$ (2D), $n > 1$ (quasi 2D), and $n = \infty$ (3D) [5]. Since the 2D perovskites have different structure, they possess unique optoelectronic properties. 2D perovskites have narrower absorption because of their larger bandgap, which depend on the number of n [5]. In addition, 2D perovskites form stable exciton at room temperature (see *Fig. 5d*) with large exciton binding energy due to the dielectric mismatch between organic and inorganic layers [5]. As a result, these properties are not ideal for photovoltaic action, leading to poor performances in solar cells [5]. Relative to 3D perovskites, 2D perovskites show remarkably higher moisture resistance (see *Fig. 5c*). This greater stability is mainly due to the hydrophobic nature of the R cation, as well as the highly oriented structure and dense packing, which reduces the density of the grain boundaries and prevents direct contact of adventitious water with the perovskite [5]. The integration of 2D perovskites into HPSCs as a stabilizer component has been recently proposed as an approach to increase the lifetimes of HPSCs.

Stable and efficient 2D/3D solar cells, is it the future?

Combining low-dimensional perovskites with 3D perovskites in layered 2D/3D composites has been proposed as a strategy to overcome the HPSC stability issue. The aim of this approach is to combine the high efficiency of 3D perovskites with the superior stability of 2D perovskites, in a synergistic

action. Several studies have demonstrated the benefits of combining 2D and 3D perovskites, and 2D/3D junctions have been used in both mesoporous solar cells and inverted architectures as shown in *Figure 6a*.

For instance, a two-step method was used for the deposition of a 3D/2D bilayer composed of MAPbI_3 and PEI_2PbI_4 [5]. As the 2D perovskite is at the top surface at the interface with the HTM (*Fig. 6a*), interfacial charge-carrier recombination is reduced and the PCE increases to >20%. These PSCs retained 85% of their initial PCE under 1 sun illumination for 800 h at 50 °C even in an ambient environment (*Fig. 6b*), providing the first example of a highly efficient and stable 3D/2D device. Importantly, this result demonstrated that it is possible to achieve enhanced stability without compromising the PCE, reaching efficiencies comparable to those of 3D PSCs. The 2D perovskite can be also developed at the bottom surface covering the TiO_2 surface while improving the electron transfer. This layered 2D/3D architecture has been implemented in standard mesoporous TiO_2 /spiro-OMeTAD solar cells as either a 3D/2D or 2D/3D active layer in an inverted configuration and in monolithic solar cells in which the HTM

and gold electrode are replaced by a carbon layer [5]. For this configuration (see *Fig. 6c*), the 2D/3D composite approach enabled a world-record stability of more than 1 year to be achieved. These devices showed no loss in performance over 10 000 h of testing (at 55 °C, 1 sun illumination for 24 h per day, sealed under ambient atmosphere).

Toxicity: towards lead free perovskites

Despite the enormous potentiality of this class of materials, 3D and 2D HP are both affected by a serious drawback due to the toxicity of lead, with the associated health and environment concerns, which can limit their commercial applications [1-5]. Despite the abundance of lead and its low percentage (about 0.1%) in final devices, its use represents a risk for the environment and an economic disadvantage for HPSC commercialization. Huge theoretical effort in screening “less toxic” materials is ongoing, however, so far, viable alternatives to Pb are only a very few due to the very stringent criteria they must have to match the performance of lead-halide perovskites. Examples include Tin (Sn) used in $\text{MASn}_x\text{Pb}_{1-x}\text{I}_3$ now reaching PCE close to 10%, but easily prone to oxidation

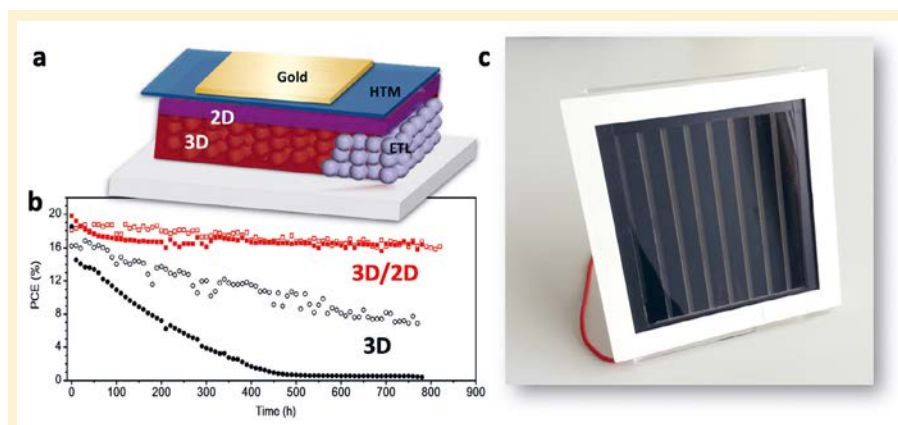


Figure 6. (a) Cartoon of the device structure based on mesoporous HPSC consisting, as an active layer, of a mixture of 3D and 2D hybrid perovskites. (b) Comparison of recent results on stability measuring the PCE under accelerating testing conditions between pure 3D perovskite and 3D/2D perovskite devices. The 2D/3D shows superior stability without sacrificing the device efficiency as reported in [5] (reprinted with permission from Springer Nature). (c) Picture of a carbon-based module 10×10 cm² developed by our group at EPFL Valais in collaboration with Solaronix.

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
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(Sn^{2+} into Sn^{4+}) or incorporated in A_2SnX_6 structures (e.g. Cs_2SnI_6), which exhibit better stability due to the presence of Sn in its stable oxidation state. Other alternatives are the “2D derivative” in the form of $\text{A}_3\text{Bi}_2\text{X}_9$ (using bismuth (Bi), X=halogen and A=MA or Cs) and the “double perovskites” such as $\text{Cs}_2\text{BB}^{3+}\text{X}_6$ (with $\text{B}^{3+}=\text{Bi}$ or Sb ; $\text{B}=\text{Cu}$, Ag , Au). Another viable option for reducing the hazards of Pb exposure is to develop effective encapsulation strategies. Pb does not pose a problem if it remains contained within the solar module; however, lead-based perovskites tend to release toxic PbI_2 by-product, possibly contaminating the environment.

Conclusions and future prospects

This article has presented a critical and inclusive summary of gradual advances, frontiers in the field of perovskite photovoltaics materials and devices, showing the main challenges and near future perspectives. Recent progress in engineering the perovskite dimensionality has been presented as an interesting new way towards efficient and stable devices. This is the next major issue which requires to be focused urgently to launch them in the market for outdoor photovoltaic applications. Interface engineering is also utmost to impart better carrier dynamics cross the solar cell junctions inclusive of charge production, transportation and extraction, and thus aids to optimize device performance.

Furthermore, bandgap engineering of perovskite materials unveiled that highly efficient HPSCs can be realized by properly tuning their bandgaps which opens applications in optoelectronics even beyond photovoltaics. Exploration of novel materials synthesis and fabrication techniques will also open the way for easy and low temperature deposition protocols, minimizing the number of steps and making it feasible for large area production. Narrow bandgap perovskite materials and plasmonic photovoltaics are expected to eventually open the door for better light harvesting strategies that will span over wide electromagnetic spectra. Toxicity due to the presence of Pb atoms still hinder their commercialization. This issue calls for an urgent effort combining theoretical screening of new materials to guide synthetic chemists and engineers in the development of alternative compounds. In addition, future research directions regarding perovskite devices should also include the development of better and deeper fundamental understanding of the structural and photophysical properties of the materials as well as of the device functioning, crucial in order to realize optimum designs. The answer, crucial for a deeper understanding and for upscale and technology uptake is still not yet-identified. Unravelling the mechanisms behind material crystallization is certainly of high interest for further tuning the material optical and electronic properties, and broaden their impact far beyond PVs. ■

FURTHER READING

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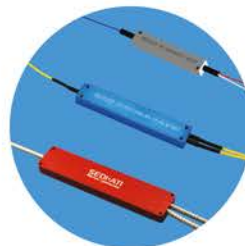
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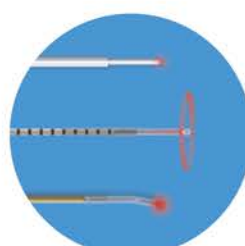
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