Review
Low-Toxicity Perovskite Applications in Carbon Electrode Perovskite Solar Cells—A Review

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Abstract: Perovskite solar cells (PSCs) with earth-abundant carbon as an effective replacer for unstable hole-transporting materials and expensive electrodes is a recently proposed structure promising better air and moisture stability. In this review paper, we report on the latest advances and state of the art of Pb-free and low-Pb-content perovskites, used as absorbers in carbon-based perovskite solar cells. The focus is on the implementation of these, environmentally friendly and non-toxic, structures in PSCs with a carbon electrode as a replacement of the noble metal electrode typically used (C-PSCs). The motivation for this study has been the great potential that C-PSCs have shown for the leap towards the commercialization of PSCs. Some of their outstanding properties include low cost, high-stability, ambient processability and compatibility with most up-scaling methods (e.g., printing). By surpassing the key obstacle of toxicity, caused by the Pb content of the highest-performing perovskites, and by combining the advantages of C-PSCs with the Pb-free perovskites low toxicity, this technology will move one step further; this review summarizes the most promising routes that have been reported so far towards that direction.

Keywords: lead-free perovskites; carbon electrode; perovskite solar cells; HTL-free; low Pb content; environmentally friendly perovskites

1. Introduction

Perovskites, which are materials with the crystal structure similar to calcium titanium oxide (CaTiO$_3$), were first discovered in 1839, when the Russian mineralogist L. A. Perovski discovered the mineral CaTiO$_3$. However, it was not until the late 1990s, when the structural dynamics of methylammonium lead iodide perovskite (MAPbI$_3$) material were studied and explored for application in optoelectronics, such as thin-film transistors, photovoltaics (PV) and light-emitting diodes [1,2]. Since then, huge leaps of progress have been made and perovskites have been implemented in high-performing solar cells [3], light-emitting diodes [4], photodetectors [5], lasers [6], as well as sensors, fuel cells, superconductors, catalysis and more [7,8].

The greatest progress and the most intensive research have been towards the application of perovskites as absorbers for solar energy conversion applications. In that direction, perovskite solar cells (PSCs) have achieved power conversion efficiencies (PCEs) that are now comparable with the traditional, well-established and widely applied technology of Si solar cells. Among the different perovskite structures, the perovskite of the organic-inorganic metal halide (OIH) group are the ones that systematically achieve the highest PCEs that are being reported. However, even though PSCs count more than 10 years of extensive study and optimizations, there is still a gap towards the commercialization of this technology. This barrier is mainly caused by three factors: (i) the reduction of PCE when moving to large area devices, (ii) the questionable stability of PSCs under real-life working conditions and (iii) the toxicity of the starting materials, most of all the lead (Pb) content.

For the up scaling of PSCs, a lot of effort has been invested in the device engineering and construction methods, which has led to large area devices with PCEs exceeding
The sources of perovskite instability include, among others, water and moisture degradation, thermal stress, light and oxygen induced degradation, ion migration and corrosion of the back contact [11]. One of the most efficient and promising methods to overcome these problems, originating from the corrosion of the metal electrode, is turning it into a different type of PSC: Carbon electrode-based Perovskite Solar Cells (C-PSCs).

In a typical structure, PSCs comprise of a multilayered device architecture of the absorber “sandwiched” between an electron transport layer (ETL) and a hole transport layer (HTL), while the circuit is completed by a metal back electrode, most commonly Au or Ag. During the long-term operation of PSCs, the migration of iodine and metals, combined with the formation of metal halide ions and oxygen vacancies, start to corrode the metal electrode, leaving the structure exposed to the environment and causing a slow degradation [12,13]. In C-PSCs, the metal electrode is replaced by a carbon (C) electrode. Carbon has an appropriate work function ($W_F$) of $-5$ eV to qualify for an efficient charge collector, while at the same time its hydrophobic nature repels oxygen and moisture from the ambient, providing a protective barrier for the perovskite layer. At the same time the inertness of C allows to remain unaffected by ion migration. This has enabled devices with long-term stability to be achieved, without the need for encapsulation [14].

Being on a track with significant advances in the aspect of overcoming the two out of three barriers which hinder the commercialization of PSCs, the remaining obstacle that needs to be tackled is the environmental and health issues caused by the toxicity of Pb and other perovskite precursor components, such as the HTL and perovskite additives. The European Union has imposed strict rules on the use of toxic elements in consumer electronics. If this problem is not resolved, the PSC technology is bound to remain in lab scale and research level. Hence, the last years have seen lots of efforts for the partial or total elimination of Pb, and its substitution by other metals, which are less toxic and environmentally and health friendly. Most of the research has been focused on the typical metal electrode structure PSCs, since it is the one that exhibits the highest PCEs so far; however, with the continuous rise of C-PSCs and their additional advantage of stability and significantly lower cost than the metal electrode PSCs, it is prominent that there needs to be a turn to low-toxicity materials' implementation in C-PSCs as well.

The aim of this manuscript is to present the applications of low-Pb-content and Pb-free perovskites in Carbon electrode Perovskite Solar Cells, in order to both inform and motivate readers towards this field of research. Initially, the design and working principles of C-PSCs will be presented, together with the current status in terms of efficiency and the state of the art devices. A general description of perovskite materials will be made, with a focus on Pb-free structures and their performance as absorbers in PSCs with metal electrode back contacts. The application of Pb-free and low-Pb-content perovskites in C-PSCs will be extensively presented and the conclusions will be based on the literature review. Finally, the prospects of low-toxicity perovskites for high-performing, stable and environmentally friendly C-PSCs will be discussed. We expect that this manuscript will enlighten the readers and will trigger the interest for further research towards non-toxic, highly stable, high-performing and low-cost C-PSCs.

2. Carbon-Based Perovskite Solar Cells (C-PSCs)

2.1. General Description

Carbon-based perovskite solar cells (C-PSCs) differ from the traditional structures in that the metal electrode is eliminated, replaced by a carbon electrode typically prepared using simple methods, such as doctor blading, screen printing and painting, by a C paste. Depending on the temperature that is required for the annealing of the C paste, in order for the electrode to form, they can be distinguished in two main categories: high-temperature (HT) and low-temperature (LT) C-PSCs. Both structures have the same working principle: upon illumination, excitons are produced by the perovskite absorbing layer, forming free charge carriers (electrons and holes); electrons are drawn to the electron transport layer (ETL) and holes are collected from the hole transport layer (HTL). The C electrode, having
an appropriate work function (W_F), similar to Au, and Fermi level above the valence band edge of the perovskite, can draw the carriers to the external circuit. Moreover, carbon has the capability to absorb oxygen and moisture, thus protecting the perovskite and providing highly stable devices. Even though the initial reports of C-PSCs achieved PCEs much lower than the conventional devices, typically below 10%, the intensive research in this field has led to optimized devices with comparable PCEs to the high-performing metal electrode PSCs, with higher stability and at a significantly lower cost (Figure 1).

![Figure 1. (a) Summary of development in PCEs of C-PSCs in comparison to state-of-the-art PSCs [15]. Reproduced with permission—Copyright 2020 Royal Society of Chemistry. (b) schematic energy level diagram of perovskite materials, TiO_2, Spiro-OMeTAD, Au and C [16]. Reproduced with permission—Copyright 2017 Wiley-VCH.](image)

2.2. High-Temperature (HT) C-PSCs

The representative HT device configuration comprises of multiple oxide layers on top of which the perovskite is deposited and formed after annealing. In particular, a compact hole blocking layer, typically TiO_2 or SnO_2 grown from precursor solutions, is first deposited on FTO glass substrates, to minimize recombination losses and prevent shunting pathways. Next, an Electron Transport Layer (ETL) is deposited, which is most commonly the wide bandgap semiconductor Titanium Dioxide (TiO_2) in a mesoporous structure, followed by an additional mesoporous layer, typically ZrO_2 or AlO_3. This layer acts as a spacer, preventing the direct contact of TiO_2 with the C electrode, which would cause a short circuiting of the device. Finally, the mesoporous C electrode is deposited from a starting C paste, which is then annealed at a high temperature to remove binders and organic substances and increase the conductivity of the resulting electrode. The perovskite precursor solution is then infiltrated through the triple mesoscopic stack and the perovskite film is formed after annealing (Figure 2). This type of devices are also referred to as “monolithic” and additionally to being HTL-free, highly stable and able to be prepared under ambient conditions, they can also be entirely prepared by printing methods, which gives an advantage when moving to up scaling.
A variety of carbon materials have been used in order to prepare high-performing C pastes, which would result in C electrodes of high conductivity, low series resistance and great mechanical stability. Among these, the combination of carbon black (CB) and graphite has been established as a high-performing formulation [18–21], while carbon nanotubes (CNTs) have also shown promising results [22,23]. In all of the highest-performing HT C-PSCs the perovskite formulations that have been used are Pb-based, with the most common being the AVAxA(1–x)PbI3, while recently efforts have turned to the incorporation of multiple cation structures, for the enhancement of performance and stability (Table 1). In the typical HT C-PSC structure, no HTL is employed; however, the state of the art PSCs of this structure have achieved PCE of 17%, when a Nickel Oxide (NiO) layer has been employed as the HTL [24], combined with a mixed cation-mixed halide perovskite (Figure 3).

Table 1. Summary table of some of the highest-performing HT C-PSCs that have been reported so far.

| PCE (%) | Perovskite | HTL | Device Configuration | Carbon Paste Formulation | Year/Reference | Comments |
|---------|------------|-----|----------------------|--------------------------|---------------|----------|
| 17.02   | Cs0.05(FA0.4MA0.6)0.95PbI2.8Br0.2 | NiO | FTO/c-TiO2/mp-TiO2/Al2O3/NiO/C | Graphite/carbon black | 2017 [24] | sequential deposition |
| 16.51   | (5-AVA)x(MA)1−xPbI3 | - | FTO/c-TiO2/mp-TiO2/ZrO2/C | Commercial C paste | 2020 [25] | PBS-X; X = Li, Na, and K post treatment of TiO2/ZrO2/C |
| 16.37   | MAPbI3 | - | FTO/c-TiO2/mp-TiO2/PbTiO3/CNTs | CNTs sprayed | 2019 [23] | ultrathin layer of ferroelectric PbTiO3 on the TiO2 scaffold |
| 16.26   | Cs0.1Rb0.05FA0.85PbI3 | - | FTO/c-TiO2/mp-TiO2/ZrO2/C | Carbon/spherical graphite | 2019 [26] | 1. DMF:DMSO: Formamidine mixed solvent 2. Evaporation control |
| 15.9    | CH3NH3PbI3(SrCl2)x | - | FTO/c-TiO2/mp-TiO2/Al2O3/C | Graphite/carbon black | 2016 [27] | SrCl2 chemical modification of perovskite |
| 15.77   | (5-AVA)x(MA)1−xPbI3 | - | FTO/c-TiO2/mp-TiO2/ZrO2/C | carbon black/graphite | 2019 [28] | VOx post-treatment of C/perovskite interface |
| 15.7    | (5-AVA)x(MA)1−xPbI3 | - | FTO/c-TiO2/mp-TiO2/ZrO2/C | Graphite/carbon black | 2018 [29] | oxygen-rich carbon black |
Table 1. Cont.

| PCE (%) | Perovskite | HTL | Device Configuration | Carbon Paste Formulation | Year/Reference | Comments |
|---------|------------|-----|----------------------|-------------------------|----------------|----------|
| 15.6    | CH₃NH₃PbI₃ | -   | FTO/c-TiO₂/mp-TiO₂/ZrO₂/C | Carbon/spheroidal graphite | 2017 [30] | 1. additive of ammonium chloride (NH₄Cl) 2. Two-step process during perovskite formation |
| 15.6    | AB-MAPbI₃ | -   | FTO/c-TiO₂/mp-TiO₂/ZrO₂/C | Graphite/ carbon black | 2017 [31] | 1. 4-(aminomethyl) benzoic acid hydroiodide (AB) organic cation 2. benzylamine hydroiodide (BA)benzylamine hydroiodide (BA) organic cation 3. 5-AVAI organic cation |
| 15.11   | (5-AVA), (MA)₁₋ₓPbI₃ | -   | FTO/c-TiO₂/mp-TiO₂/ZrO₂/C | Graphite/ carbon black | 2019 [32] | 1. Ethanol co-solvent in GBL |
| 15.03   | CH₃NH₃PbI₃ | NiO | FTO/c-TiO₂/mp-TiO₂/Al₂O₃/NiO/C | Graphite/ carbon black | 2015 [33] | quadruple-layer architecture |
| 15      | CH₃NH₃PbI₃ | -   | FTO/c-TiO₂/mp-TiO₂/Al₂O₃/C | Graphite/ carbon black | 2017 [34] | 1. NMP solvent 2. slow crystallization (SC) method |
| 15      | Cs₀.₁FA₀.₉PbI₃ | -   | FTO/c-TiO₂/mp-TiO₂/ZrO₂/C | Commercial C paste | 2019 [35] | Prepared in glove box |
| 14.9    | CH₃NH₃PbI₃ | NiO | FTO/c-TiO₂/mp-TiO₂/ZrO₂/NiO/C | Graphite/ carbon black | 2015 [36] | sequential deposition |
| 14.7    | CH₃NH₃PbI₃ | -   | FTO/c-TiO₂/mp-TiO₂/Al₂O₃/C | SWCNTs/carbon black | 2016 [22] | SWCNT-doped graphite/carbon black electrode |
| 14.5    | MAPbI₃₋ₓClₓ | -   | FTO/c-TiO₂/mp-TiO₂/ZrO₂/C | Carbon/spheroidal graphite | 2018 [37] | Addition of 0.45M MACl increases PCE from 8.74% to 14.5% |
| 14.5    | CH₃NH₃PbI₃ | -   | FTO/c-TiO₂/mp-TiO₂/ZrO₂/C | N/A | 2016 [38] | Effect of LiCl additive |
| 14.3    | (5-AVA)$_x$(MA)$_{(1-x)}$PbI₃ | -   | FTO/c-TiO₂/mp-TiO₂/ZrO₂/C | Commercial C paste | 2017 [39] | humidity assisted thermal exposure (HTE) as a post-treatment method—150 h |
| 14.27   | CH₃NH₃PbI₃-xGuCl | -   | FTO/c-TiO₂/mp-TiO₂/ZrO₂/C | Commercial C paste | 2016 [40] | 1. Additive GuCl in perovskite 2. Voc 1.02V |
| 14.2    | CH₃NH₃I | NiO | FTO/c-TiO₂/mp-TiO₂/ZrO₂/NiO/C | carbon black/graphite | 2015 [41] | 1. NiO nanosheet paste on ZrO₂ 2. Comparison of nanoparticles and nanosheets. 3. Screen printed device |
2.3. Low-Temperature (LT) C-PSCs

The low-temperature C-PSC configuration, besides the obvious difference of the C paste requiring a low-temperature annealing to form the C electrode, differs from the HT in two major aspects: (a) the C electrode is deposited after the perovskite deposition and crystallization on the appropriate substrate and (b) the mesoporous layers can be omitted and replaced by planar ones. Particularly for the spacer layer, this can be entirely eliminated, since the perovskite layer intervenes between the C electrode and the ETL, thus preventing a short circuit at this interface. This type of devices are also referred to as “paintable” (Figure 4).

Figure 4. (a) Schematic illustrating the cell architecture [42]. Reprinted with permission from Zhang, F.; Yang, X.; Wang, H.; Cheng, M.; Zhao, J.; Sun, L. ACS Appl. Mater. Interfaces 2014, 6, 16140–16146—Copyright 2014 American Chemical Society and (b) fabrication process of LT “paintable” perovskite solar cells [43]. Reproduced with permission—Copyright 2016 Wiley-VCH.

The carbon pastes that are being used typically consist of carbon black, graphite, polymer, additive and a non-polar solvent. In this type of C-PSC, it is crucial that the components of the paste are compatible with the underlying perovskite layer, in order to avoid its decomposition. It is noteworthy that this architecture benefits the use of free-standing electrodes as well as electrodes that are simply press transferred on the perovskite layer, giving the opportunity for high efficiency devices with an ease of fabrication and an extremely low cost [44–47]. Additionally, in this structure the perovskite is grown directly on the ETL, avoiding the infiltration through multiple mesoporous layers. This gives a much higher flexibility and a variety of choices for the perovskite structures to be used. This has led to devices with PCEs comparable to the ones of Au-based devices, owing to the potential of multiple cation, multiple halide perovskites for high-performance and high-stability devices, as summarized in Table 2. The current state-of-the-art LT C-PSC has achieved PCE of 19.2%, in devices with self-standing C films used as counter electrode, mixed cation perovskite structure and spiro-OMeTAD as the HTM [44] (Figure 5).

Figure 3. (a) Schematic architecture of the C-PSC consisting of FTO glass as a transparent substrate, a compact TiO₂ layer, a mesoporous TiO₂ layer, an Al₂O₃ layer and NiO layer coated with graphite/carbon black CE; (b) cross section SEM image of device with TiO₂/Al₂O₃/NiO/C (Cs₀.₅(FA₀.₄MA₀.₆)₀.₉₅PbI₂.₈Br₀.₂) structure; (c) I-V curves of champion perovskite solar cell devices under standard AM 1.5G illumination at 100 mWcm⁻² [24]. Reproduced with permission—Copyright 2017 Royal Society of Chemistry.
Table 2. Summary table of some of the highest-performing LT C-PSCs that have been reported so far.

| PCE (%) | Perovskite | HTL | Device Configuration | Carbon Paste Formulation | Year/Reference | Comments |
|---------|------------|-----|----------------------|--------------------------|----------------|----------|
| 19.2    | (FA<sub>0.75</sub>MA<sub>0.25</sub>)PbI<sub>2.75</sub>Br<sub>0.25</sub> | spiro-OMeTAD | FTO/c-TiO<sub>2</sub>/mp-TiO<sub>2</sub>/perovskite/spiro-OMeTAD/C | Commercial C paste | 2018 [44] | self-standing films |
| 18.65   | Cs<sub>0.05</sub>(MA<sub>0.17</sub>FA<sub>0.83</sub>)<sub>0.95</sub>Pb(I<sub>0.83</sub>Br<sub>0.17</sub>)<sub>3</sub> | spiro-OMeTAD | FTO/c-TiO<sub>2</sub>/mp-TiO<sub>2</sub>/perovskite/spiro-OMeTAD/C | Graphene in IPA | 2019 [48] | various commercial carbon sources (carbon black, graphite sheet, and graphite) studied |
| 18.22   | FA<sub>0.3</sub>MA<sub>0.7</sub>PbI<sub>3</sub> | P3HT/graphene | FTO/SnO<sub>2</sub>/TiO<sub>2</sub>/perovskite/P3HT/C | C in propylene glycol monomethyl ether acetate | 2019 [49] | Stability 89% of original PCE after 600 h |
| 18.1    | (FA<sub>0.83</sub>MA<sub>0.17</sub>)PbI<sub>2.15</sub>Br<sub>0.85</sub> | CuSCN | FTO/c-TiO<sub>2</sub>/mp-TiO<sub>2</sub>/perovskite/CuSCN/C | Graphitic carbon layer | 2019 [50] | ≈95% of their initial efficiencies for >2000 h under full-sun illumination |
| 17.78   | Cs<sub>0.05</sub>(MA<sub>0.17</sub>FA<sub>0.83</sub>)<sub>0.95</sub>Pb(I<sub>0.83</sub>Br<sub>0.17</sub>)<sub>3</sub> | CuPc | FTO/ZnSnO<sub>2</sub>/perovskite/CuPc/C | Commercial C paste | 2019 [51] | Zn-doped SnO<sub>2</sub> ETL |
| 17.58   | Cs<sub>0.05</sub>(FA<sub>0.83</sub>MA<sub>0.17</sub>)<sub>0.95</sub>Pb(I<sub>0.83</sub>Br<sub>0.17</sub>)<sub>3</sub> | CuSCN | FTO/c-TiO<sub>2</sub>/mp-TiO<sub>2</sub>/perovskite/CuSCN/C | MWCNTs in chlorobenzene | 2019 [52] | 1. MWCNTs to replace carbon black 2. Stability 80% after 1000h 1 sun illumination |
| 17.56   | FACsPbI<sub>3</sub> | spiro-OMeTAD | ITO/SnO<sub>2</sub>/perovskite/spiro-OMeTAD/C | free-standing CNT sheet | 2018 [46] | Trifluoromethanesulfonic acid vapor doping of the free-standing CNT sheet enabled tuning of conductivity and work function of electrode |
| 17.46   | Cs<sub>0.05</sub>(FA<sub>0.4</sub>MA<sub>0.6</sub>)<sub>0.95</sub>Pb<sub>2.4</sub>Br<sub>0.2</sub> | CuPc | FTO/NiTiO<sub>2</sub>/perovskite/CuPc/C | Commercial C paste | 2018 [53] | 1. planar 2. Ni-doped rutile TiO<sub>2</sub> as electron transport layer |
| 17.02   | Cs<sub>0.05</sub>(FA<sub>0.85</sub>MA<sub>0.15</sub>)<sub>0.95</sub>Pb(I<sub>0.85</sub>Br<sub>0.15</sub>)<sub>3</sub> | spiro-OMeTAD | FTO/SnO<sub>2</sub>/perovskite/spiro-OMeTAD/C | Self-adhesive carbon film | 2020 [45] | 1. planar 2. graphite paper/carbon film electrode |
Table 2. Cont.

| PCE (%) | Perovskite | HTL | Device Configuration | Carbon Paste Formulation | Year/Reference | Comments |
|---------|------------|-----|----------------------|--------------------------|-----------------|----------|
| 16.6    | Cs0.05(AM0.17FA0.83)0.95Pb(I0.83Br0.17)3 | spiro-OMeTAD | FTO/c-TiO2/m-TiO2/perovskite/C | SWCNT film | 2017 [54] | 1. press-transferred single-walled carbon nanotube (SWCNT) film infiltrated with Spiro-OMeTAD 2. superior long-term stability at elevated temperatures |
| 16.25   | FAxMA1−xPbIyBr3−y | - | ITO/SnO2/MWCNTs:perovskite/C | Commercial C paste | 2019 [55] | 1. MWCNTs additive in the perovskite solution 2. all air processed 3. stability 93% under ambient air conditions for 22 weeks |
| 16.2    | MAPbI3:MAPbI4Br3−x | - | FTO/c-TiO2/m-TiO2/perovskite/C | Commercial C paste | 2019 [56] | MAPbI3/MAPbI4Br3−x perovskite stacking structure |
| 16.1    | MAPbI3 | CuPc | FTO/c-TiO2/m-TiO2/perovskite/CuPc/C | Commercial C paste | 2016 [57] | 8.5% drop during 600 h durability tests |
| 16.03   | MAPbI3 | - | ITO/HMB:C60/perovskite/C | Commercial C paste | 2019 [58] | 1. hexamethonium bromide-doped fullerene C60 ETL 2. No hysteresis |
| 15.73   | CH3NH3PbI3-SWCNT | - | FTO/c-TiO2/m-TiO2/perovskite/SWCNT-C | flaky graphite/spheroidal graphite/carbon black | 2019 [59] | 1. SWCNTs in both anti-solvent and C electrode 2. stability of 90 days in dark under high humidity and high-temperature conditions |
| PCE (%) | Perovskite                  | HTL | Device Configuration                          | Carbon Paste Formulation          | Year/Reference | Comments                                                                 |
|---------|-----------------------------|-----|-----------------------------------------------|-----------------------------------|----------------|---------------------------------------------------------------------------|
| 15.6    | Cs$_{0.05}$MA$_{0.16}$FA$_{0.79}$Pb(I$_{0.84}$Br$_{0.16}$)$_3$ | -   | FTO/c-TiO$_2$/m-TiO$_2$/perovskite/PEA$_2$PbI$_4$/C | Commercial C paste                | 2018 [60]      | 1. 2D perovskite interlayer 2. Stability 92% of initial PCE after 1000 h of exposure to ambient conditions |
| 15.38   | MAPbI$_3$                   | -   | FTO/C$_{60}$/perovskite/C                    | Commercial C paste                | 2018 [61]      | 1. First report on fullerene ETL 2. Additional replacement of FTO with graphene based TC electrode |
| 15.29   | Cs$_{0.04}$(MA$_{0.17}$FA$_{0.83}$)$_{0.96}$Pb(I$_{0.83}$Br$_{0.17}$)$_3$ spiro-OMeTAD | -   | FTO/c-TiO$_2$/m-TiO$_2$/perovskite/C+spiro-OMeTAD | Commercial C paste                | 2016 [62]      | Carbon cloth embedded in C paste electrode                               |
| 15.27   | MAPbI$_3$:MA$_{1-x}$Cs$_x$PbI$_3$ | -   | FTO/c-TiO$_2$/m-TiO$_2$/perovskite/C         | Graphite/carbon black             | 2020 [63]      | Post treatment with acetate salts (CsAc, FAAc, MAAc, KAc, NaAc)            |
| 15.23   | MAPbI$_3$                   | -   | FTO/c-TiO$_2$/m-TiO$_2$/m-Al$_2$O$_3$/perovskite/C | MWCNTs in chlorobenzene          | 2017 [64]      | Boron doping of MWCNTs for enhanced hole extraction                        |
As the interest in C-PSCs is rising, so are the PCE values that are achieved and C-PSCs have now been established as the most promising structure for large-area applications and potential commercialization of perovskite solar modules, owing to their high stability, capability to be processed entirely under ambient conditions, the ability to be HTL-free and, most importantly, their significantly lower cost compared to PSCs with metal electrodes. Hence, it is expected that more progress will be presented in the near years to come. One of the most challenging tasks will be to implement environmentally friendly perovskite structures in C-PSCs, in order to overcome the additional barrier of PSCs towards their commercialization, which are the toxicity issues caused by the Pb content of the perovskite.

3. Perovskites
3.1. General Description—Current State of the Art

Hybrid organic-inorganic lead halide perovskites are compounds with the general chemical formula ABX$_3$ and octahedral structure. A is the component that generally forms the unit cell and is an organic monocation, typically CH$_3$NH$_3^+$ (methylammonium-MA), HC(NH$_2$)$_2^+$ (formamidinium-FA) or the inorganic cesium (Cs$^+$). Component B is a smaller than A, divalent metal cation, most commonly Pb$^{2+}$ or Sn$^{2+}$, which is located in the center of the cube unit cell, and X is an anion, typically a halogen such as Cl$^-$, Br$^-$ or I$^-$ (Figure 6).

Figure 6. The ABX$_3$ perovskite crystal structure and the atomic structure of three A site cations explored. B is Pb or Sn, and X is a halogen ion [65]. Reproduced with permission—Copyright 2014 Royal Society of Chemistry. On the right side the energy level diagram, showing the processes occurring during a PSC of the normal structure operation is depicted.

Organic-inorganic hybrid perovskites possess optoelectronic properties that make them suitable for applications as photoactive materials in solar cells. These features include high absorptivity, high charge carrier mobility, long exciton diffusion length, tunable bandgap and low exciton binding energy. The CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbBr$_3$ perovskites were first studied and presented as sensitzers in Dye Sensitized Solar Cells (DSSCs) which demonstrated moderate PCE of 3.81% [66]. After that, device engineering,
materials composition and chemical modifications have enabled PCEs to rise rapidly and reach 25.5% in 2021 [67], 12 years after their first appearance in the solar cell community. The highest-performing devices, exhibiting PCEs that exceed 20%, employ MA and/or FA as the A cation and Pb as the B cation. Even though the performance of the perovskite based SCs is now comparable in terms of efficiency and stability with Si SCs, at the same time with a much lower cost, there is a major issue towards the commercialization and real-life application of this technology that needs to be tackled, and this is the toxicity and environmental harmfulness of Pb. Especially in consumer electrical and electronic equipment, the use of hazardous materials is prohibited and considering that Pb has been identified as one of the ten hazardous chemicals listed by ROHS in order to avoid its exposure to environment and people, it is mandatory that its use is limited [68,69] (Figure 7). Thus, Pb-based perovskites are unlikely to see a broad industrialization in order to compete with other photovoltaic technologies, unless there is turn to lead-free perovskite materials that would provide stable devices with acceptable PCEs, without endangering the human health and the environment [70].

Towards that direction, the most promising candidates that have been investigated as substitutes of Pb are Tin (Sn), Germanium (Ge), Bismuth (Bi), Antimony (Sb) and Copper (Cu).

- Tin (Sn)

Tin is considered to be the most suitable candidate for Pb substitution, because of its similar valence electronic configuration and ionic radius (Sn$^{2+}$ = 115 pm and Pb$^{2+}$ = 119 pm) [72]. Sn-based perovskites have the general formula of ASnX$_3$, A being MA$^+$, Fa$^+$ or Cs$^+$ cation, and X a halogen anion. They have optical bandgap of 1.2–1.6 eV which is appropriate for light absorbing applications and are characterized by large carrier mobilities and low exciton binding energies [73]. The highest PCEs obtained with Sn-based perovskites is 13.24% in an ITO/PEDOT:PSS/perovskite/C60/BCP/Ag device configuration, with the (FA$_{1-x}$EA$_x$)$_{0.98}$EDA$_{0.01}$SnI$_3$ perovskite and 12.96% in a c-TiO$_2$/absorber/spiro-OMeTAD/Au, with CsSnI$_3$ perovskite quantum rods [74,75] (Figure 8).

Figure 7. Schematic illustration of (a) effect of exposure of toxic-lead on human life and (b–d) factors responsible for the perovskite degradation [71]. Reproduced with permission—Copyright 2019 Wiley-VCH.
Germanium (Ge)

Germanium is another element with valence electronic configuration similar to Pb$_2^+$, that qualifies as a potential substitute for low-toxicity PSCs. The ionic radius is 73 pm, which is smaller than Pb and Sn and it possesses analogous electronegativity with Sn; however, it gets more easily oxidized, which makes its handling demanding [70]. The most promising candidates for Ge-based PSCs are ammonium halides (AGeX$_3$), such as methylammonium germanium triiodide (MAGeI$_3$), and cesium germanium triiodide (CsGeI$_3$), owing to their suitable optical bandgap of 1.9 and 1.6 eV, respectively, combined with excellent hole and electron conducting behavior and better stability in ambient conditions than MAPbI$_3$ [78,79]. The PCEs obtained so far with Ge-based perovskites in PSCs still lay below 1%, in particular 0.57% with MAGeI$_2$Br$_{0.3}$ [80]; however, a PCS of 7.11% has been reported in a mixed Sn-Ge perovskite, CsSn$_{0.5}$Ge$_{0.5}$I$_3$, and the FTO/PCBM/perovskite/spiro-OMeTAD/Au device structure [81] (Figure 9).

Figure 8. (a) Tolerance factor of a series of common perovskites [76] Reprinted with permission—Copyright 2015 Royal Society of Chemistry; Efficiency progress of (b) Sn-based and (c) low-bandgap Sn–Pb mixed PSCs [77]. Reproduced with permission—Copyright 2021 Royal Society of Chemistry.

Figure 9. (a) SEM image of a FIB processed cross-section and J-V curve of an optimized MAGeI$_2$Br$_{0.3}$ based solar cell [80] Reprinted with permission from Kopacic, I.; Friesenbichler, B.; Hoeffler, S.F.; Kunert, B.; Plank, H.; Rath, T.; Trimmel, G. ACS Appl. Energy Mater. 2018, 1, 343–347—Copyright 2018 American Chemical Society; (b) energy-level diagram of the mixed Sn-Ge perovskite based device and (c) stabilized power output of the Sn-Ge PSC [81]. Reproduced with permission from Chen, M.; Ju, M.-G.; Garces, H.F.; Carl, A.D.; Ono, L.K.; Hawash, Z.; Zhang, Y.; Shen, T.; Qi, Y.; Grimm, R.L.; et al. Nat. Commun. 2019, 10, 16—Copyright 2019 Springer Nature.
• Bismuth (Bi)

Bismuth materials (Bi), with the structure of A$_3$Bi$_2$X$_9$ have also drawn significant attention as non-toxic substitutes for Pb, because of their similar electronic configuration, very close ionic radius of 103 pm (Pb = 119 pm) and a good value of electronegativity. They typically consist of A cations of MA$^+$, Cs$^+$, Rb$^+$, K$^+$, guanidinium, cyclohexylammonium or imidazolium to form a 0D perovskite structure [82]. The highest PCE recorded so far is of the order of 3.59%, in a Cs$_3$Bi$_2$I$_9$-Ag$_3$Bi$_2$I$_9$ bulk heterojunction (BHJ) perovskite solar cell (Figure 10).

Figure 10. (a) Schematic structure of FTO/c-TiO$_2$/mp-TiO$_2$/photoactive film/PDBD-T/Au device; (b) J-V curves of the champion devices based on different photoactive films; (c) J-V curves of the devices based on 0.5Cs$_3$Bi$_2$I$_9$-Ag$_3$Bi$_2$I$_9$ blend films [83]. Adapted with permission—Copyright 2020 Elsevier.

• Antimony (Sb)

Following Bi, antimony (Sb) based perovskites have been evaluated as photoactive materials, since they also exhibit appropriate optoelectronic properties to qualify as efficient absorbers for PSCs. They have the general structure of A$_3$Sb$_2$X$_9$, A being an organic or inorganic cation and X a halogen, while the cation and anion species combination determines the structure and dimensions. The antimony cation has a similar valence electronic configuration with Pb, even though it appears in a trivalent state; therefore, it might exhibit long carrier lifetimes. When incorporated in PSCs, Sb-based perovskites have so far achieved low PCEs, the highest being 3.34%, in a FTO/0.5Cs$_3$Bi$_2$I$_9$-Ag$_3$Bi$_2$I$_9$/spiro-OMeTAD/Au device configuration, using the MA$_3$Sb$_2$I$_9$-Cl$_x$ perovskite. The PSCs retain 90% of the initial PCE after being stored under ambient conditions for over 1400 h and additionally, semitransparent Sb-based PSCs have been demonstrated with PCEs from 2.62 to 3.06% indicating the great potential for building integrated applications [84] (Figure 11).

Figure 11. (a) Schematic drawing of the semitransparent device architecture of glass/FTO/c-TiO$_2$/m-TiO$_2$/MA$_3$Sb$_2$I$_9$-Cl$_x$/spiro-OMeTAD/Au; (b) J-V curves of the semitransparent PSCs with different full-device AVTs, obtained using ∼20 nm Au electrodes. The insets are photographs of the as-fabricated semitransparent PSCs (Reprinted with permission from Yang, Y.; Liu, C.; Cai, M.; Liao, Y.; Ding, Y.; Ma, S.; Liu, X.; Guli, M.; Dai, S.; Nazaruddin, M.K. ACS Appl. Mater. Interfaces 2020, 12, 17062–17069, Copyright 2020, American Chemical Society) [84].
• Copper (Cu)

Finally, copper (Cu), has also emerged as promising for photovoltaic applications. Because of the small ionic radius (73 pm), layered 2D perovskite structures can be formed, with general formula \((\text{RNH}_3)_2\text{CuX}_4\) where \(\text{RNH}_3^+\) is an aliphatic or aromatic cation and \(X\) is a halogen. The highest PCE obtained so far is 2.41%, in a FTO/TiO\(_2\)/perovskite/Spiro-OMeTAD/Au device configuration and \((\text{CH}_3\text{NH}_3)_2\text{CuCl}_4\) perovskite [85] (Figure 12).

![Figure 12. Summary of the highest reported PCE of Pb-free perovskites applied in PSCs with metal back contact.](image)

3.2. Pb-Free Perovskites in C-PSCs

As briefly aforementioned, among the various divalent metal cation candidates to replace lead for environmentally friendly PSCs, Sn has emerged as the most promising alternative due to its similarity of optoelectronic properties, coordination geometry and, mainly, owing to the high efficiency achieved in photovoltaic devices, up to 13.24%, which is the highest PCE obtained up to date in lead-free PSCs [74]. Sn(II)-based perovskites exhibit greater absorption coefficients and higher charge-carrier mobilities than conventional Pb(II)-based counterparts, making them very attractive not only for lead-free solar cells, but also for other applications, such as photodetectors, light-emitting diodes, lasers and phototransistors [86,87]. However, these tin-containing materials present low stability due to the extreme sensibility of Sn\(_2^+\) cations to oxygen, which can be spontaneously oxidized into Sn\(_4^+\) in ambient atmosphere. When this occurs, undesirable high conductivity (p-doping) and Sn vacancies are produced, leading to increased carrier recombination that results in poor device performance and low reproducibility of Sn-PSCs [88,89]. In this regard, most efforts have aimed at minimizing the intrinsic oxidation of Sn\(_2^+\) to Sn\(_4^+\) by using specific Sn\(_2^+\)-rich conditions (excess of tin halide) or appropriate reducing agents during the film preparation. Beside this, other approaches as solvent/additive engineering or perovskite compositional strategies, which focus on modifying A/B site cations and X site anions, have been also widely used to modulate the perovskite film morphology and improve its photoelectric performances [77]. Main group VA metals such as Bi and Sb exist as trivalent cations in halide perovskites and derivatives and are distinguished for their high chemical stability. Moreover, they are less toxic than both Pb and Sn, while at the same time they are also widely available from natural sources. These ions have similar structural and electronic properties (electronic configuration, electronegativity and ionic radius) with Pb, hence they are promising candidates for applications in Pb-free PSCs [90]. The typical structure of Bi halide and Sb halide based compounds is \(\text{A}_3\text{B}_2\text{X}_6\), and depending on the combinations, there can be a dimensional regulation (0 D, 1 D and 2 D) of these materials in crystal structures with tunable optoelectronic properties. Additionally, double perovskite structures, with the general formula of \(\text{A}_2\text{B}_3\text{X}_6\), form three dimensional (3D) corner-sharing perovskite structures, and perovskite derivatives...
of the formula $A_2BIBIIIX_6$, form three-dimensional (3D) corner-sharing perovskites. The value of 1.97 eV and a simultaneous blue shift in the optical spectra. On the contrary, the absorption band for MASnIBrCl experienced a significant redshift around 850 nm, with a narrower bandgap of 1.49 eV. An additional increase in the SnCl$_2$ content yielded to formation of rudorffite structures which are 3D based on edge-shared [AX$_6$] and [BX$_6$] octahedra (Figure 13).

Figure 13. Crystal structures of group VA metal halide based perovskites and derivatives [90–93].

Appropriate material combinations, such as MA$_3$Bi$_2$I$_9$, Cs$_3$Bi$_2$I$_9$, MA$_3$Sb$_2$I$_6$ and Cs$_3$Sb$_2$I$_9$ have provided PSCs with PCE values up to 3.2% for Bi halide based PSCs [94], 2.84% for Bi halide double perovskite based PSCs [95], 4.7% for antimony halide based PSCs [96] and 5.51% for rudorffite structure PSCs [97]. Despite their modest efficiencies, these materials exhibited high absorption coefficients and are much more air-stable than their lead counterparts. The best performing PSCs comprise a HTL and a metal back electrode (Au or Ag); however, with the increasing turn towards C-PSCs, some efforts to employ these materials in PSCs with C electrode have also been presented in the last few years, and more are expected to arise in the future.

3.2.1. Tin (Sn)-Based Perovskites

Hybrid Organic-Inorganic (HOI) Sn-Based Perovskites

Tsai et al. [98] reported in 2017 the only existing example in the literature where a methylammonium (MA) tin halide is used as an active material in carbon-electrode perovskite solar cells (C-PSC). In their work, a series of methylammonium organotin mixed-trihalide (MASnIBr$_{2-x}$Cl$_x$) perovskites have been prepared, by varying the ratio of SnCl$_2$/SnBr$_2$. The synthesized perovskites have been thoroughly studied as per their structural and optical properties. The equimolecular precursor mixture of MAI and an optimized ratio 10/90 of SnCl$_2$/SnBr$_2$ allowed the incorporation of a small quantity of Cl$^-$ ion in the tin perovskite lattice, when Br$^-$ ions occupied more than 50% of the halide site ($x \leq 0.5$). If otherwise, the Br proportion was lower ($x > 0.5$), phase separation could take place to form MASnI$_{2-x}$Br$_x$ and MASnBr$_2$Cl$_{3-2x}$. The starting perovskite MASnIBr$_2$ (SnCl$_2$/SnBr$_2$ 0/100) had an optical bandgap of 1.81 eV with absorption at 700 nm. By increasing the SnCl$_2$ amount up to 25% there is an increase in the bandgap, which reached the value of 1.97 eV and a simultaneous blue shift in the optical spectra. On the contrary, once an equimolecular mixture of tin bromide/chloride was reached (SnCl$_2$/SnBr$_2$ 50/50), the absorption band for MASnIBrCl experienced a significant redshift around 850 nm, with a narrower bandgap of 1.49 eV. An additional increase in the SnCl$_2$ content yielded to
further shifts on the absorption bands, giving rise to much smaller bandgap of 1.25 eV at 100% SnCl2 (Figure 14).

![Absorbance and Voltage](image)

**Figure 14.** (a) The synthetic approach and absorption spectra of mixed halide tin-based perovskites deposited on glass substrates with corresponding proportions of the SnCl2/SnBr2: (a) 0/100; (b) 10/90; (c) 25/75; (d) 50/50; (e) 75/25; (f) 100/0; (b) potential-energy diagrams (energies in eV with respect to vacuum) of mixed-halide tin-perovskite films with halide ratios controlled on mixing MAI and SnCl2/SnBr2 precursors in SnCl2/SnBr2 proportions varied as indicated; (c) current–voltage curves of carbon-based mixed halide tin-perovskite devices; (d) efficiency stability profiles of the encapsulated devices as a function of storage period [98]. Reproduced with permission—Copyright 2017 Wiley.

The optimal composition of MASnIBr1.8Cl0.2 (that is, SnCl2 10%), was then incorporated as the active layer, in HT C-PSCs of the FTO/TiO2/Al2O3/perovskite/C configuration, reaching a PCE of 3.1%, along with prolonged environmental stability than the control MASnIBr2 perovskite (SnCl2 0%). It was resulted that by adding a small amount of Cl in the perovskite precursor led to delayed charge recombination and increased the exciton lifetime, leading to improved photovoltaic performance of the mixed trihalide Sn perovskites, compared to the bihalide analogs. It should be noted that the perovskite preparation process was performed in inert ambient conditions. Formamidinium tin halide (FASnI3) perovskite has been extensively used in PSCs, owing to the higher stability compared to the methylammonium-based perovskite counterparts [99,100]; however, when it comes to C-PSCs, only few mentions exist.

Recently, Mohammadian-Sarcheshmeh et al. [101] presented HTM-free, FASnI3 C-PSCs with improved device performance and stability. This was achieved by the addition of antioxidant uric acid (UA) in the perovskite precursor to retard the oxidation of Sn2+. The UA addition did not provoke any special changes in the absorption wavelength, implying that the UA molecules are not incorporated in the perovskite lattice. However, an increase in the absorbance intensity was noted, which indicates an improvement in the quality and crystallinity of the perovskite films, with the maximum recorded for 10% UA content. This was also confirmed by XRD measurements, where the 10% UA containing FASnI3 showed higher perovskite peak intensities indicating better crystallinity (Figure 15). This effect was further verified by SEM pictures, where the FASnI3 + 10% UA perovskite clearly provides
films which are more uniform and pin-hole free. It was suggested that this is a result of a decreased crystal growth rate after the addition of UA. Finally, the UA perovskites were implemented in HT C-PSCs with the FTO/TiO₂/Al₂O₃/perovskite/C structure and a champion PCE of 1.2% was achieved for the FASnI₃ + 10% UA perovskite based device (Figure 15).

Figure 15. (a) Absorbance for cells with the different percent of UA added to FASnI₃ solution; (b) XRD patterns of the FASnI₃ and FASnI₃ with 10% UA; (c) J-V curves for the cells involving FASnI₃ (1) and FASnI₃ 10% UA (2) [101]. Reproduced with permission—Copyright 2020 Elsevier.

Superhalide BF₄⁻ anions, have been previously used to improve the optoelectronic properties of organic—inorganic hybrid lead-PSCs [102,103], by being incorporated in the FASnI₃ lattice. Based on these results, Rameez et al. developed a series of novel mixed halide-superhalide FASnI₃-x(BF₄)ₓ perovskites (denoted as FBS), and implemented them in HT C-PSCs [104]. In their work the tetrafluoroborate ions that were added in the precursor solutions, partially replaced the iodide anions at the X-site and tuned the perovskite structure. The presence of fluorine atoms, which can form strong Sn-F bonds due to their high electronegative, justifies the superior photovoltaic parameters observed for these (super)halide-modified tin solar cells (FBS). Although diverse attempts were made to synthesize FSB films with different ratios of BF₄⁻ : I⁻, DFT calculations confirmed the successful preparation of only FASnI(BF₄)₂ (x = 2), which met the appropriate Goldschmidt tolerance factors and showed the characteristic XRD peaks of tin perovskites at 14.0°, 24.3°, 28.2°, that matched with the theoretical values. In contrast, these X-ray diffraction patterns were not experimentally observed when x = 1 or x = 3, revealing that stable FBS perovskite films were not formed in those cases. The FASnI(BF₄)₂ film showed stronger optical absorption than the reference FASnI₃, as depicted in Figure 16. A red shift was noted at the edge of the visible spectral region, from an initial value of 890 nm (E₂g = 1.40 ± 0.01 eV) for FASnI₃ to higher values of around 910 nm (E₂g = 1.36 ± 0.01 eV) for FSB. The authors suggested that the partial inclusion of BF₄⁻ into the perovskite lattice, whose ionic radius is greater (232 pm) than that of the I⁻ (215 pm), could be responsible for this decrease in the optical band gap which resulted in an improvement of the corresponding HT C-PSC device performance. The champion FBS device, whose precursor solution was prepared from an equimolecular mixture Sn(BF₄)₂ and FAI, exhibited at PCE of 1.3% with enhanced stability, both under light-soaking and dark storage conditions, compared to the control FASnI₃ perovskite (Figure 16). Moreover, FBS films showed better reproducibility than that of standard FASnI₃.
Figure 16. (a) Thin-film XRD patterns of FASnI$_{3-x}$(BF$_4$)$_x$ controlled by stoichiometric proportions with various BF$_4^-$ sources as indicated. Chemical notations appear above the spectra; (b) absorption (solid curves) and normalized PL (dashed curves) spectra of FSB and FASnI$_3$ films deposited on glass substrates; (c) J-V curves for the best FASnI$_3$ and FSB cell; (d) light-soaking effect measured under ambient conditions [104]. Adapted with permission from Rameez, M.; Shahbazi, S.; Raghunath, P.; Lin, M.C.; Hung, C.H.; Diau, E.W.G. J. Phys. Chem. Lett. 2020, 11, 2443–2448. Copyright 2020 American Chemical Society.

Further investigation led the same research group to publish a parallel study that describes the incorporation of thiocyanate anion (SCN$^-$) into the 3D FASnI$_3$ lattice to stabilize the tin perovskite [105]. In their work series of novel FASnI$_{3-x}$(SCN)$_x$ (x = 0, 1, 2, or 3) perovskites have been synthesized and implemented in HT C-PSCs of the FTO/TiO$_2$/Al$_2$O$_3$/perovskite/C structure. Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD) measurements proved that the ambident nucleophile SCN$^-$, whose negative charge is delocalized over its π-conjugated electronic system, behaves as a bridging ligand assisting the formation of a strong three-dimensional octahedral network.

The 3D-octahedral crystal geometry is preserved owing to the smaller size of Sn$^{2+}$ in relation to Pb$^{2+}$ that implies only minimal alterations in the Goldschmidt tolerance factor. The band gaps of FASnI$_2$(SCN) (x = 1) and FASnI(SCN)$_2$ (x = 2), with values of 1.36 and 1.38 eV, respectively, were found to be narrower than those of the pristine FASnI$_3$. The FASnI(SCN)$_2$ (x = 2) was found to have the optimal crystal structure geometry, leading to PCE of 2.4% (Figure 17). The improvement in the photovoltaic performance is ascribed to a greater interaction in the modified thiocyanate-containing tin perovskite, between Sn and pseudohalide SCN$^-$, with respect to the Sn-I binding, which consequently led to a decreased metal oxidation, retarded charge carrier recombination as well as greater moisture and oxygen tolerance.
Figure 17. (a) DFT simulated crystal structure of FASnI(3−x)(SCN)x (x = 0–3) showing that a three dimensional network is formed by corner-sharing SnX$_6$ octahedra with FA$^+$ occupying the interstitial voids; (b) energy diagrams (energy/eV with respect to vacuum) of films with FASnI(3−x)(SCN)$_x$ (x = 0–3); (c) representative J-V characteristics of each FASnI(3−x)(SCN)$_x$ (x = 0–3) device [105]. Adapted with permission from Rameez, M.; Lin, E.Y.R.; Raghunath, P.; Narra, S.; Song, D.; Lin, M.C.; Hung, C.H.; Diau, E.W.G. ACS Appl. Mater. Interfaces 2020, 12, 21739–21747. Copyright 2020 American Chemical Society.

Driven by previous reports of phenethylammonium iodide (PEAI) and ethylenediammonium iodide (EDAI) that have been used as additives of the thiocyanate-containing Pb-based perovskites [106,107], the authors investigated these compounds as coadditives in the optimized Sn-based FASnI(SCN)$_2$ perovskite, which further improved the PCE to 3.7%, used a combination of 10%PEAI and 5%EDAI, in HT C-PSCs with NiO as a hole transporting layer.

Reduced-Dimensionality HOI Sn-Based Perovskites

In addition to the different HOIP discussed above, additional references to low-dimensional Sn-based perovskites for mesoscopic HT C-PSC have also been made. In one of them, the use of the cation organic spacer 2-hydroxyethylammonium (HEA) has been reported as a method to control the structure of the corresponding perovskite obtained, HEAxFA$_{1-x}$SnI$_3$ (x = 0–1) [108], according to the content of HEA$^+$ ions incorporated into the crystal lattice. For this study, a range of SnI$_2$ and HEAI/FAI precursor mixtures were prepared in varied proportions and tested as absorber layers. It was noted that when the bifunctional HEA cation was systematically incorporated into the perovskite, the geometry underwent successive modifications, going from orthorhombic (x = 0; $E_g$ 1.36 eV) to rhombohedral (x = 0.2 and 0.4; $E_g$ 1.45 and 1.53 eV, respectively) and then to a tetragonal 3D-structure with vacancies when x ≥ 0.6 ($E_g$ 1.77–2.07 eV), which eventually turned to the thermodynamically preferred 2D-orthorhombic and monoclinic structures, when x = 1 (HEA 100%) (Figure 18).
As verified from the experimental data, the HEA⁺ possesses the ability to tune the bandgap, giving rise to the aforementioned continuous changes in the perovskite crystal structure. As a result, the optoelectronic properties were improved and, consequently, also the performance of the photovoltaic device, achieving a maximum PCE of 2.5% when \( x = 0.4 \) (HEAI 40%), in a HT C-PSC with the structure FTO/TiO₂/Al₂O₃/perovskite/C. Further optimization in the fabrication process, by introducing a second solvent-extraction (SE) step, with 3% EDAI₂, led to an improved PCE of 3.7%, with negligible hysteresis (Figure 18). Low dimensional (2D) Dion–Jacobson (DJ) Sn-based perovskites, were first applied in printable HT C-PSCs of the FTO/TiO₂/ZrO₂/perovskite/C structure by Chen et al. [109]. The films of the 4AMP)(FA)\(_{n-1}\)Sn\(_n\)I\(_{3n+1}\) (n = 1–4) perovskites, prepared by the simple solution-casting method, where 4-(aminomethyl)piperidinium (4AMP) is an insulating organic spacer cation, presented absorption spectra with an edge at 860 nm and strong steady-state photoluminescence (PL) peak at 840 nm, corresponding to an optical bandgap of 1.47 eV, when \( n = 4 \). Significantly longer PL lifetime was also recorded, compared to other Sn-based perovskite materials, suggesting a superior performance when implemented in photovoltaic devices. Indeed, a promising PCE of 4.22% has been obtained, in C-PSCs with Voc values that can be tuned by changing the \( n \) values, giving enough space for further improvement in C-PSCs based on DJ Sn(II)-based perovskites. Moreover, the devices exhibited a good stability, with only 9% of PCE decay after 100 h of sun exposure (Figure 19).
Inorganic Sn-Based Perovskites

The first report of all-inorganic Sn-based perovskites application in C-PSCs was presented by Li and co-workers in 2016 [110]. In this work, in order to overcome the problem of Sn^{2+} fast oxidation in the presence of oxygen and moisture and to suppress the Sn vacancy-induced recombination, the authors used hypophosphorous acid (HPA) as a reducing agent. The HPA was inserted as an additive in the CsSnIBr_2 perovskite precursor solution to stabilize the precursor. The generation of new compounds after the addition of HPA was confirmed by the slight enhancement of light absorption on the 500–750 nm range, as well as by zeta potential analyzer which showed a trend of cluster enlargement with increasing HPA concentration. Perovskite films prepared on TiO_2/Al_2O_3 substrates exhibited bandgap of 1.63 eV and a slightly extended towards the infrared region band edge, resulting from lower trap densities. By implementing the perovskite precursor solutions in C-PSCs of the TiO_2/AlO_3/perovskite/C structure, by infiltration, an increase in the PCE from 1.7% to 3% was achieved, along with negligible hysteresis and a notable stability (Figure 20).

Finally, Zhang and co-workers recently conducted a study with similar approach, by creating a reducing environment through the employment of electron-rich cobaltocene (CoCP_2) as an electron donor to neutralize the unwanted Sn^{4+} cations present in the CsSnI_3 perovskite precursor solution [111]. The addition of CoCP_2 resulted in films with low hole trap density, low oxidation degree, low p-type doping state and high electron density (Figure 21). Consequently, when the perovskite was implemented in fully printable HT C-PSCs, employing NiO as the HTL (TiO_2/Al_2O_3/perovskite/NiO/C configuration) an optimal PCE of 3.0% was obtained, which is remarkably higher than 0.65% for the reference device.
Figure 21. (a) Dark J-V curves of the hole-only devices for the CsSnI$_3$ film without and with CoCp$_2$. The inset shows the equation determining the trap state density; (b) J-V curves of CsSnI$_3$ PSCs with and without CoCp$_2$ under illumination and (c) under dark [111]. Reproduced with permission—Copyright 2020 Royal Society of Chemistry.

3.2.2. Bismuth Based Perovskites

The first report on organic-inorganic iodobismuthates, in C-PSCs was in 2017, by Li et al. [112]. In this work the organic cations of pyridinium [py] and methyl pyridinium [mepy] combined with the one dimensional [BiI$_4$]$^-$ anion have been used to synthesize and analyze the organic-inorganic [py] [BiI$_4$] and [mepy] [BiI$_4$] perovskites. The band gap values of [py] [BiI$_4$] and [mepy] [BiI$_4$] in the powder form were found to be 1.98 eV and 2.17 eV, respectively, with the values being calculated with both diffuse reflectance spectra and electrochemically and in good comparison with each other. Moreover, these values correlate well with the values obtained by simulation (DFT calculations). The 2 perovskites were then incorporated in C-PSCs of the triple mesoscopic structure, where the perovskite was infiltrated into the TiO$_2$/ZrO$_2$/C mesoporous scaffold and heated at 40 °C overnight. The champion device, with PCE of 0.9%, was achieved with the pyridinium cation.

It was found that [py] [BiI$_4$] starts to crystallize on the surface of the carbon before it can reach TiO$_2$, which resulted in poor reproducibility of the devices; however, this problem could be resolved by optimizing the solvents in the precursor solution and by carefully controlling the deposition conditions. In addition, the [py] [BiI$_4$] films exhibited a good stability under ambient conditions, with no structural changes observed at the XRD patterns after one week of exposure to air. The [mepy] [BiI$_4$] perovskite on the other hand did not present any photovoltaic effect, which was attributed to the poor crystallization in the mesoscopic structure, low carrier density and relatively large bandgap. Even though the PCE demonstrated was poor, this study indicated that attention needs to be paid in the cation site, when studying the potential of Bi based perovskites for solar cell applications (Figure 22).

Moving their work one step further, the same group have performed a study of different organic cations, namely thiazolium, aminothiazolium and imidazolium, in new structures of organic-inorganic iodobismuthates [113]. In their work, 0D organic–inorganic bismuth-halide compounds, thiazolium bismuth iodide [TH$_3$][Bi$_2$I$_6$], imidazolium bismuth iodide [IM$_3$][Bi$_2$I$_6$] and 1D 2-aminothiazolium bismuth iodide [AT][BiI$_4$] have been synthesized and studied as crystalline materials, as thin-films, and in solar cell devices. Direct band gap values of 2.08 eV, 1.78 eV and 2.00 eV have been determined for [TH$_3$][Bi$_2$I$_6$], [AT][BiI$_4$] and [IM$_3$][Bi$_2$I$_6$], respectively, indicating that the only promising structure is the [AT][BiI$_4$]. This structure has been further tested as a photovoltaic material in HTL-free C-PSCs of the triple mesoscopic structure, exhibiting PCE of 0.47%. Moreover, no obvious structural changes were observed after two weeks exposure to air in the dark, indicating high stability of all three compounds (Figure 23).
Moving their work one step further, the same group have investigated the influence of under layers for the optimization of iodobismuthate perovskite C-PSCs [111]. Reproduced with permission—Copyright 2020 Royal Society of Chemistry.

In 2017, (CH₃NH₃)₃Bi₂I₉ PSCs have also been reported, in a LT (low-temperature) C paste device architecture. The authors studied the effect of substrate and deposition methods on the performance of (CH₃NH₃)₃Bi₂I₉ PSCs [114]. For this purpose, compact and mesoporous TiO₂ films have been prepared and the non-toxic, Bi based perovskite has been deposited using a single step or a two-step process, which has been reported for the first time in iodobismuthate perovskites. The results highlighted the key role of the compact TiO₂ layer in the charge transport, photoelectron collection and recombination processes, hence the performance of Bi based C-PSCs.

The films that were fabricated using the two step method achieved superior coverage both on the compact and mesoporous TiO₂ layers, however, the highest PCE (0.054%) was obtained with the one step deposition. The mesoscopic devices presented superior performance compared to the planar devices, owing mainly to the higher photocurrent.

Figure 22. (a) Intermolecular interactions (shown in orange lines) in [py] [BiI₄] (top) and [mepy] [BiI₄] (bottom) unit cells. Image generated by VESTA (Visualization for Electronic and Structural Analysis) software. Bismuth atoms: magenta; iodine atoms: cyan; carbon atoms: brown; nitrogen atoms: violet; (b) Tauc plots and bandgap estimations for [py] [BiI₄] (magenta) and [mepy] [BiI₄] (navy), powder samples diluted in BaSO₄; (c) Boltzmann-fitted J-V curves of the [py] [BiI₄] champion cell [112]. Reproduced from T. Li, Y. Hu, C. A. Morrison, W. Wu, H. Han and N. Robertson, Sustainable Energy Fuels 2017, 1, 308—Published by The Royal Society of Chemistry.

Figure 23. Powder XRD patterns on thin films of [TH] [Bi₂I₉] (a), [AT] [Bi₂I₉] (b) and [IM] [Bi₂I₉] (c) annealed at different temperatures comparing to the theoretical patterns predicted from the single-crystal XRD (blue); (d) Tauc plots from diffuse reflectance measurements; (e) energy level diagram including other components in the solar cell [113]. Reproduced from T. Li, Q. Wang, G. S. Nichol, C. A. Morrison, H. Han, Y. Hu and N. Robertson, Dalton Trans. 2018, 47, 7050—Published by The Royal Society of Chemistry.
obtained and the significantly higher recombination resistance that these devices exhibited. The champion device maintained 92.6% of its initial PCE after 32 days of storage in ambient air. Even though the PCEs obtained are very low, this study has shed light on the influence of under layers for the optimization of iodobismuthate perovskite C-PSCs (Figure 24). One year later, the study of a series of cations in the ABi₃I₁₀ (A = MA, FA, and Cs) perovskite structure in C-PSCs, using a LT C paste was reported [115]. After a thorough band gap tuning, PCE of 1.51% has been obtained with the inorganic CsBi₃I₁₀ as a photoactive layer, combined with excellent ambient stability over 30 days. All films, MABi₃I₁₀ (MBI), FABi₃I₁₀ (FBI) and CsBi₃I₁₀ (CBI) have exhibited a typical triclinic crystalline structure; however, CsBi₃I₁₀ has exhibited the strongest XRD peaks ((003) and (006) at 12.8° and 25.25°). In good agreement with the XRD results, the morphology of the CBI film was more uniform and dense than those of the MBI and FBI films. Direct band gaps of CBI, MBI, and FBI have been calculated to be 1.76, 1.78, and 1.81 eV, respectively, and the corresponding HTL-free C-PSCs exhibited PCEs of 1.51, 0.67 and 0.87%. Moreover, all the devices retained over 85% of their original efficiency after 30 days, clearly demonstrating the excellent stability of the Bi perovskites in C-PSCs and highlighting their prospects.

By modifying the solvent involved in the precursor solution and by employing a hole transport material, the PCE of \((\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9\) perovskite has been further improved, reaching 1.62% [116]. More specifically, the non-toxic solvent methylacetate has been used in the perovskite precursor solution, while two different HTMs have been investigated: the conventional Spiro-OMeTAD (2,2′,7,7′-tetrakis(N,N′-di-p-methoxyphenylamino)-9,9′-spirobiuorene) and P3HT-poly (3-hexylthiophene-2,5-diyl). The C electrode has been deposited on top of the perovskite/HTM, by doctor blading a LT C paste. The XRD measurements have confirmed the single-crystalline phase of the resulting perovskite and the formation of high quality films, while the band gap has been calculated to be \(-2.1\) eV. A high PL density observed also supports the formation of a good quality MBI films. Furthermore, the \((\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9\) perovskite, prepared from a precursor solution of methyl acetate, has been implemented in C-PSCs as the active layer, followed by the two HTMs under study. Both spiro-OMeTAD and P3HT devices presented hysteresis-free J-V curves.

Figure 24. (top) Scheme of the fabrication process of the MBI layer based on the c-TiO₂ and m-TiO₂ (bottom) (a) XRD patterns of different BiI₃ and MBI films; (b) absorption spectrum of different MBI films and Tauc plots for the MBI thin film; (c) J–V characteristics of PSCs based on different device architecture and MBI-fabricated method, under 1 sun illumination [114]. Reproduced from M. Kong, H. Hu, L. Wan, M. Chen, Y. Gan, J. Wang, F. Chen, B. Dong, D. Eder and S. Wang, RSC Adv. 2017, 7, 35549—Published by The Royal Society of Chemistry.
and PCEs of 1.12% and 1.62%, respectively. The higher performance of P3HT is mainly attributed to the improved Voc values, and has been ascribed to a more deep HOMO level of P3HT (−3.5 eV) compared to Spiro-OMeTAD (−2.22) that blocks holes more effectively. In addition, P3HT PSCs exhibited improved stability, when subjected to accelerated test of continuous 1 sun (100 mW/cm², AM 1.5) illumination without use of UV-filters for 840 h (35 days). While the Spiro-OMeTAD PSCs showed rapid decrease in PCE from 1.12% to 0.7% in only 245 h (10 days), the devices with P3HT showed a negligible drop of 0.2% in PCE. The hygroscopic nature of Spiro-OMeTAD has been identified as the main cause of that instability (Figure 25).

Another class of perovskites that has recently been developed is the “double perovskites”. This perovskite structure, of general formula \( \text{A}_2(\text{BB'})_6\text{O}_{12} \), where \( \text{A} \) stands for an alkali metal and \( \text{B}, \text{B'} \) are transition metals of the first and second (or third) rows, is called “double” because the unit cell is twice that of perovskite. It has the same architecture of 12 coordinate \( \text{A} \) sites and 6 coordinate \( \text{B} \) sites, but two cations are ordered on the \( \text{B} \) site. By modulating the \( \text{B} \) and \( \text{B'} \) species, some promising compounds have been discovered, potentially able to replace Pb based perovskites. Among them, the all-inorganic \( \text{Cs}_2\text{AgBiBr}_6 \) has emerged as the most promising, owing to the long radiative emission lifetime and high tolerance to heat and humidity. In a very interesting work, Li et al. have employed a variety of alkali metal ions (\( \text{Li}^+, \text{Na}^+, \text{K}^+ \) and \( \text{Rb}^+ \)) to regulate the crystal lattice of \( \text{Cs}_2\text{AgBiBr}_6 \) perovskites [117]. XPS characterization has revealed that the alkali metal ions are successfully doped into the perovskite crystal lattice, owing to the smaller ionic radius of \( \text{Li}^+ \) (0.76 Å), \( \text{Na}^+ \) (1.02 Å), \( \text{K}^+ \) (1.38 Å) and \( \text{Rb}^+ \) (1.52 Å) compared to other cations. This was expected to contribute to the elimination of intrinsic defect, thus promoting the
photovoltaic efficiency. At the same time, SEM pictures have revealed that alkali metal doped perovskite yields dense and pinhole-free films, with a smoother morphology, while the Kelvin probe force microscopy (KPFM) images revealed increased electronic chemical potentials of alkali metal ions doped perovskite films, which is an indication of better charge extraction and less recombination.

The alkali metal doped perovskites were then incorporated in HTM free, C-PSCs, employing a LT C paste. The highest PCE was obtained for the Li doped perovskite and it was 2.57%, which is the highest obtained so far in double perovskite C-PSCs. In addition, the devices retained 80% of their initial efficiency after 90 days (25 °C, 5% RH) and 60 days (85 °C, 0% RH) storage, demonstrating a superior tolerance to environmental conditions (Figure 26). Finally, the type of lead-free perovskites, also called ruddorfite, with the Ag$_2$BiI$_5$ structure, have been used as a replacement of Pb based perovskites in C-PSCs employing a LT C-paste [118]. Even though the Voc values obtained are adequate (770 mV) the PCE remains below 1%, mainly due to the low current density values, suggesting that this structure still needs a lot of effort and improvement.

![Figure 26.](image-url)

**Figure 26.** (a) The diagram and (b) cross-sectional SEM image of a typical Cs$_2$AgBiBr$_6$ PSC; (c) illustration of energy alignment diagram; (d) J-V curves; (e) IPCE spectra; evolution of photovoltaic performances for pristine (black line) and Li$^+$ tailored (red line) PSCs free of encapsulation under 25 °C, 5% RH (f) and 85 °C, 0% RH conditions (g) [117]. Reprinted with permission from Li, J.; Duan, J.; Du, J.; Yang, X.; Wang, Y.; Yang, P.; Duan, Y.; Tang, Q. *ACS Appl. Mater. Interfaces* **2020**, *12*, 47408–47415. Copyright 2020 American Chemical Society.

### 3.2.3. Antimony Based Perovskites

The structural, electronic and optical properties of antimony-copper double perovskites have been investigated, by using first-principles density functional theory (DFT) calculations [119] in order to estimate their potential for applications in optoelectronics and photovoltaics. For this purpose, a group of 18 Pb-free inorganic and hybrid double perovskites ASbCuX$_6$ (A = Cs$_2$, MA$_2$, FA$_2$, CsMA, CsFA, MAFA; X = I, Br, Cl) was evaluated to obtain suitable perovskites for photovoltaic technology. Replacing Cs with MA
or FA has led to a calculated increase in the unit cell volume, which is a useful finding for tuning the properties of a group of compounds to obtain the characteristics that are desired for specific applications. The lowest formation enthalpies were calculated to be for (FA)$_2$SbCuCl$_6$ (−114.2 kJ/mol), (MAFA)SbCuCl$_6$ (−1093 kJ/mol) and (MA)$_2$SbCuCl$_6$ (−1070.6 kJ/mol). The more negative calculated formation enthalpies suggest that the hypothetical perovskites in consideration are likely to be stable; hence these structures are expected to yield the most stable devices as well. The estimated band gap values for the double perovskites range from 1 eV to 2 eV, highlighting the suitability of the materials for photovoltaic applications. Moreover, the band gap of the double perovskites can easily be tuned by changing the halogen content, while the considered Pb-free double perovskites were found to be indirect band gap semiconductors. The optical absorption of the 18 non-toxic double perovskites under investigation have been calculated and the results of the investigations have shown a high absorption for solar radiation (0.49–4.12 eV), making the compounds suitable for solar energy conversion applications. Even though this study has brought out the potential of double perovskites, these have not yet been applied in C-PSCs.

So far there has only been one report of antimony perovskites applied in C-PSCs, by Xiang et al. [120], where Sb was used as a dopant in the inorganic CsPbI$_3$ perovskite, to enhance the phase stability and improve the perovskite film morphology. Sb atoms were chosen because of their small size, which allows for them to be inserted into the α-CsPbI$_3$ crystal lattice. This was suggested by the authors to induce crystal lattice distortion and contribute to the enhancement of the α-CsPbI$_3$ phase stability. A small amount, 2–4% of Sb doping provided films with a smoother surface and decreased grain size. The absorption spectra, on the other hand, did not present any changes after the doping. The Sb doped CsPb$_{0.96}$Sb$_{0.04}$I$_3$ perovskite was then implemented in HTL-free C-PSCs, where the C electrode was painted on the perovskite layer. The devices exhibited increased performance compared to the CsPbI$_3$ C-PSCs, with PCE as high as 5.31% vs. 4.45% for CsPbI$_3$, while hysteresis has also been significantly reduced. More importantly, CsPb$_{0.96}$Sb$_{0.04}$I$_3$ C-PSCs showed remarkable stability in air atmosphere, retaining 93% of their initial PCE after 37 days (Figure 27).

![Figure 27](image)

Figure 27. (a) J–V curves of the C-PSCs based on α-CsPbI$_3$ and CsPb$_{0.96}$Sb$_{0.04}$I$_3$ films under forward and reverse scans; (b) stability results. Change of the normalized PCE of the non-encapsulated CsPb$_{0.96}$Sb$_{0.04}$I$_3$ and CsPbI$_3$ C-PSCs with time. The devices were stored in an air atmosphere at room temperature and measured periodically in an ambient environment [120]. Reproduced with permission—Copyright 2018 Royal Society of Chemistry.

3.2.4. Other Structures

Other elements that have been tested in order to replace Pb in non-toxic Pb-free perovskites include iron (Fe), copper (Cu) and manganese (Mn).

Yin et al. [121] have been prepared and characterized CH$_3$NH$_3$FeCl$_4$ (MAFeCl$_4$) single crystals and films. The structure of the MAFeCl$_4$ single crystal presented many differences compared to the MAPbI$_3$. Initially, MAFeCl$_4$ was proven to not having the perovskite structure. Secondly, the valence of Fe in MAFeCl$_4$ is +3, while Pb has valences
of +2 or +4. Finally, the band gap of MAFeCl₄ was determined to be 2.15 eV, which is significantly different from that of MAPbI₃, and much higher than the optimal for use in solar cells, indicating a moderate performance when implemented in PSCs. Indeed, MAFeCl₄ was used as the active layer in PSCs with a low-temperature C paste painted over the MAFeCl₄ and the PCE obtained was 0.054%, with the main factor restricting the performance being the very low photocurrent density values (Figure 28). However, the authors further tested the photoelectric response of the MAFeCl₄ device under 330 nm illumination with different chopping-frequencies and found that the best response was at 1.33 Hz, which highlights the potential of these devices in other electronic applications, such as piezoelectric and magnetic.

![Figure 28](image_url)

Figure 28. (a) The position of iron in the periodic table of elements and schematic diagrams of the unit cell structure in ball-stick type and polyhedron type; (b) Kubelka-Munk spectrum of MAFeCl₄ and (c) the best J–V curve of the FTO/TiO₂/MAFeCl₄/carbon electrode device under AM 1.5 (100 mW/cm²) [121]. Reproduced by J. Yin, S. Shi, J. Wei, G. He, L. Fan, J. Guo, K. Zhang, W. Xu, C. Yuan, Y. Wang, L. Wang, X. Pu, W. Li, D. Zhang, J. Wang, X. Ren, H. Ma, X. Shao and H. Zhou, RSC Adv. 2018, 8, 19958–19964. Copyright 2018 The Royal Society of Chemistry.

Being inspired by the investigation of metal-organic frameworks, and in particular the enhancement of their moisture stability using hydrophobic groups, in combination with the rising report on layered hybrid perovskites, such as [C₆H₅(CH₂)₈NH₃(CH₃NH₃)₂Pb₃I₁₀, which also present a high stability, Li et al. have reported a lead-free, highly stable C₆H₄NH₂CuBr₂I compound for solar cell applications [122]. The films prepared with this novel compound presented a high optical absorption through the entire visible solar emission spectrum, while the bandgap has been estimated to be ~1.64 eV, and the photoluminescence (PL) peaked at ~1.50 eV. These results reveal that C₆H₄NH₂CuBr₂I is a promising light absorber (Figure 29). A high absorption coefficient was also obtained from the transmission spectrum, together with a high electron mobility of ~2 × 10⁻¹ cm² V⁻¹ S⁻¹ and negative Hall coefficient, which indicates that the carriers are n-type.

![Figure 29](image_url)

Figure 29. (a) Pawley fit of XRD of C₆H₄NH₂CuBr₂I observed (black) and calculated (red) diffraction pattern. The green line is the difference between the observed and calculated patterns; (b) UV/Vis spectroscopy of C₆H₄NH₂CuBr₂I thin film. Inset shows a picture of the thin film; (c) Tauc plot from UV/Vis spectroscopy to determine E_g under the assumption of direct band gap and photoluminescence spectra [122]. Reprinted with permission from Li, X.; Zhong, X.; Hu, Y.; Li, B.; Sheng, Y.; Zhang, Y.; Weng, C.; Feng, M.; Han, H.; Wang, J. J. Phys. Chem. Lett. 2017, 8, 1804–1809. Copyright 2017 American Chemical Society.
An additional interesting property of the C₆H₄NH₂CuBr₂I compound has also been highlighted and this regards the stability of the material in water, where the films remained black after their direct contact, contrary to the CH₃NH₃PbI₃ perovskite that decomposes immediately upon contact with water. This was confirmed by both the UV/vis absorption spectrum measurements that were performed before and after dropping water on the film surface, where no changes were observed and by the XRD patterns that remained the same after 4 h of water soaking. This is a very important finding which concerns the stability of resulting solar cells in humid environments, as well as the potential for fabrication in ambient conditions. The authors ascribed this exceptional water stability to the incorporation of hydrophobic groups in the structure. The copper based compound was then used as the light absorber in printable C-PSCs of the triple mesoscopic structure and the best performing device yielded PCE of 0.46% in forward scanning mode and a much higher PCE of 2% in reverse scanning mode. Even though the PCE values are only modest and the hysteresis is large, the authors suggested that this could be further optimized after the incorporation of a HTL in the devices. C-PSCs without HTL take advantage of the ambipolarity of CH₃NH₃PbI₃ perovskites; however, in the case of C₆H₄NH₂CuBr₂I there appears to be only n-type behavior of the material. Moreover, the minimizing of the Cu⁺ formation during the film processing, which causes additional pathways for recombination could improve the C-PSCs efficiency further. Overall the Cu-based compound has shown great potential for its use in C-PSCs with high water stability (Figure 30).

In order to study the photoresponse of organic–inorganic hybrid manganese perovskite (CH₃NH₃)₂MnCl₄ for optoelectronic applications, Nie et al. [123] have prepared thin films, using a solution process and incorporated them in PSCs, with a doctor bladed C electrode back contact. Initially, films were prepared on TiO₂ substrates and presented a preferential growth oriented along the b-axis direction on the TiO₂ surface. The devices that were fabricated showed an evident, even though low, photoresponse with a maximum photocurrent density of 148 nA/cm². The low performance was attributed to interfacial mismatch and it was suggested that the incorporation of a HTL would reduce the interfacial recombination giving rise to the photocurrent generated by the device. The most
interesting part of this study, though, was that the devices exhibited a strong absorption in wavelengths below 420 nm (332, 357 and 418 nm) which is an evidence of ultraviolet photoresponse. This could be very useful for preparing optical recorders or optical memory devices, even though it is not favorable for application in solar cells.

Finally, Pt has also been explored as a replacement of Pb, in n–i–p solar cells with the structure F:SnO$_2$/CdS/Cs$_2$PtI$_6$/carbon/Cu that have shown promising device efficiency of 13.88% [124]. The authors have reported for the first time Pt-based photoabsorber Cs$_2$PtI$_6$ which has been synthesized by atmospheric solution processing from CsI and PtI$_4$ precursors in a mixture of solvents. Cs$_2$PtI$_6$ has exhibited a favorable bandgap of 1.4 eV and hole mobility value of 62.6 cm$^2$/(Vs)$^{-1}$. Despite the promising PCE of these devices the high cost of Pt together with the use of Cu as an additional back contact would make the cost of such PSCs restricting for large area applications. However, it is demonstrated that Pt provides an excellent model system for the replacement of Pb, owing to its high atomic number, oxidation resistance, and stability. Moreover, Cs$_2$PtI$_6$ appeared to be in a stable phase for 1000 h, under AM1.5G at 65 °C.

3.3. Low-Toxicity Mixed X-Pb Perovskites in C-PSCs

Apart from the structures that are entirely free from Pb, additional structures where a portion of Pb has been substituted with a low-toxicity metal appear to be interesting, since they manage to reduce the harmfulness of the resulting devices, by simultaneously retaining a lot of the reference Pb-based device performance. Among these, the alloyed mixed Sn-Pb perovskites have been widely studied. These structures have the advantage of being less toxic than Pb-based perovskites and at the same time the tin self-doping oxidation is suppressed, while the band gap is tuned to lower values, closer to the optimum bandgap of 1.34 eV, according to the Shockley-Queisser limit. In metal electrode based PSCs, PCEs that exceed 18% have been reported for Sn-Pb perovskites, while their use in tandem all perovskite devices has achieved PCEs > 25% [125,126].

In C-PSCs, the first report of mixed Pb-X perovskites was in 2016 [127] by Tsai et al. In this work, alloyed Sn-Pb mixed-halide perovskites of the CH$_3$NH$_3$Sn$_y$Pb$_{1-y}$I$_{3-x}$Cl$_{x}$ structure were synthesized and studied. In both single halide and mixed halide perovskites, the absorption spectra presented a shift towards longer wavelengths and consequently the bandgap showed a decreasing trend, with increasing Sn content, as shown in Figure 24. From XRD measurements it was demonstrated that Cl doping (25% SnCl$_2$) promotes shrinking of the size of the unit cell and changes the crystal from the tetragonal structure to the orthorhombic structure. Additionally, it was found that incorporating 25% Sn in perovskite led to an increased work function and binding energy. In terms of PCE, it was demonstrated that both the device performance and stability were significantly improved when Sn precursor SnI$_2$ was replaced with SnCl$_2$. The optimum proportion of 75% of SnCl$_2$ showed PCE of 2.15%, which was increased to 4.35% with the addition of 30 mol % SnF$_2$. By further introducing a NiO HTL, in a HT C-PSC device configuration of FTO/TiO$_2$/Al$_2$O$_3$/NiO/C, with the CH$_3$NH$_3$Sn$_{0.75}$Pb$_{0.25}$I$_{3-x}$Cl$_x$ perovskite, the PCE reached a maximum value of 5.13% (Figure 31).

The all-inorganic perovskite CsPb$_{0.9}$Sn$_{0.1}$I$_2$Br$_3$ has been implemented in C-PSCs using a LT C paste and the FTO/c-TiO$_2$/mp-TiO$_2$/perovskite/C device configuration. The devices have exhibited an outstanding Voc of 1.26V and PCE of 11.33% [128]. In addition, the all-inorganic PSCs exhibited a good long-term stability and resistivity against heat and moisture. Despite the promising results, it is still controversial on how low-toxicity this formulation is, considering that the Pb amount that has been substituted by Sn is only 10% mol (Figure 32).
Figure 31. (a) Absorption spectra of CH$_3$NH$_3$SnyPb$_{1-y}$I$_{3-x}$Cl$_x$ films deposited on glass substrates with Sn/Pb ratios ($y = 0$–$1$) controlled by the stoichiometric proportions of the SnCl$_2$/PbI$_2$ precursors summarized at the top; (b) histogram of PCE with 17 identical CH$_3$NH$_3$SnyPb$_{0.75}$Pb$_{0.25}$I$_{3-x}$Cl$_x$ devices fabricated under the same experimental conditions, which gives an average PCE $5.0 \pm 0.1\%$ and a maximum PCE $5.13\%$ [127]. Reprinted with permission by Tsai, C.M.; Wu, H.P.; Chang, S.T.; Huang, C.F.; Wang, C.H.; Narra, S.; Yang, Y.W.; Wang, C.L.; Hung, C.H.; Diau, E.W.G. ACS Energy Lett. 2016, 1, 1086–1093. Copyright 2016 American Chemical Society.

Figure 32. (a) Energy level diagrams of all-inorganic PSCs; (b) J-V plots of all-inorganic PSCs based on CsPbBr$_3$, CsPbI$_2$, and CsPb$_{0.9}$Sn$_{0.1}$I$_2$Br$_2$; (c) Normalized PCE retentions of encapsulated CsPb$_{0.9}$Sn$_{0.1}$I$_2$Br$_2$ based all-inorganic PSCs kept at RT; (d) Normalized PCE retentions of encapsulated CsPb$_{0.9}$Sn$_{0.1}$I$_2$Br$_2$ based all-inorganic PSCs and MAPbI$_3$/C based PSCs continuously heated at $100^\circ$C [128]. Reprinted with permission by Liang, J.; Zhao, P.; Wang, C.; Wang, Y.; Hu, Y.; Zhu, G.; Ma, L.; Liu, J.; Jin, Z. J. Am. Chem. Soc. 2017, 139. Copyright 2017 American Chemical Society.

In 2020, CsPb$_{0.5}$Sn$_{0.5}$I$_2$Br was proposed to realize high-efficiency PSCs. By using antioxidant tea polyphenol (TP) the authors have managed to obtain high quality and stable inorganic perovskite films, that were then incorporated in HT C-PSCs of the TiO$_2$/Al$_2$O$_3$/NiO/C architecture, which exhibited an impressive PCE of 8.1% [124]. Apart from low bandgap Sn-Pb mixed perovskites, there have been some interesting reports on Pb substitutes, alternative to Sn, e.g. Zinc (Zn) and Manganese (Mn). In particular, an impressive PCE of 15.37% has been recorded for CH$_3$NH$_3$Pb$_2$Zn$_{1-x}$I$_3$ perovskite, which has been implemented in HT C-PSCs of the FTO/c-TiO$_2$/mp-TiO$_2$/ZrO$_2$/C architecture; however, considering that the optimum performance has been with 1% of Zn, it can be considered that Zn is rather a dopant than a Pb substitute. Finally, CsPb$_{0.995}$Mn$_{0.005}$I$_{1.01}$Br$_{1.99}$ has also demonstrated
highly stable C-PSCs, with PCE of 7.36%, but question about the toxicity of this structure still remain.

4. Conclusions

Carbon electrode based perovskite solar cells (C-PSCs) have shown great potential over the last years, obtaining solar conversion devices with power conversion efficiencies (PCEs) which are now close to the metal electrode based PSCs, while at the same time they possess superior stability and a significantly lower cost of production. Additionally, they are the type of PSCs which are the most likely to achieve a viable consumer product, given their compatibility with scalable fabrication methods. In order to overcome the final drawback towards the commercialization of this technology, which is the high toxicity originating from the Pb content of the highest-performing hybrid organic-inorganic perovskites (HOIP) most commonly used, research is now starting to turn to Pb-free and low-Pb-content perovskite formulations. Among these, the most promising alternative, which is Sn, is highly challenging due to the tendency of Sn$^{2+}$ to quickly being oxidized upon contact with oxygen and moisture. Some interesting methods to minimize this effect have been reported, one of them being the inclusion of superhalides, such as BF$_4^-$ or PF$_6^-$, or other anions such as the polyatomic pseudohalide SCN$^-$. Moreover, it was suggested that by tailoring the band gaps through the modification of the crystal structures using a combination of organic cations (e.g., HEA/FA and 4(AMP)/FA) the optoelectronic properties of Sn-based PSCs could be improved, contributing to the additional increase in efficiencies.

On the other hand, some alternative approaches for Pb-free C-PSCs include Bismuth (Bi)-based perovskites that have achieved a maximum PCE of 2.57% and Antimony (Sb)-based perovskites that have achieved PCE of 5.31%, along with superior stability. Other structures, such as Iron (Fe), Copper (Cu) and Manganese (Mn) have also been presented and even though the PCEs remain low, these structures exhibit some highly promising properties, which are high photoelectric response, high water stability and UV photoresponse, which make them interesting for further investigation.

The highest PCE obtained so far in C-PSCs has been of 8.1%, in a mixed Pb-Sn structure; however, even though the content of Pb is lower in the mixed perovskite than the pure Pb based, the toxicity issues originating from both metals still exist.

Overall, the successful implementation of Pb-free and low-Pb-content perovskites in PSCs with a carbon electrode is still a challenging task and needs a lot of optimization in order to achieve devices with acceptable PCEs. Despite the challenges though, to obtain a high-performing PSC which would be metal electrode-free, HTL-free, low-cost, highly stable and at the same time Pb-free would mark the beginning of a new era towards the large-scale application of perovskite solar modules and the leap from the laboratory to the commercial application of a technology that has been extensively studied over more than a decade and is at a crucial point of evolvement.

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