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## **Chlorides, other Halides and Pseudo-halides as Additives for the Fabrication of Efficient and Stable Perovskite Solar Cells**

Fei Cheng,<sup>[a]</sup> Jie Zhang\*<sup>[b]</sup> and Thierry Pauporté\*<sup>[a]</sup>

*[b] Dr J. Zhang*

*The Key Lab of Fuel Cell Technology of Guangdong Province, Guangdong, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, 510640, China.*

*E-mail : [cejzhang@scut.edu.cn](mailto:cejzhang@scut.edu.cn);*

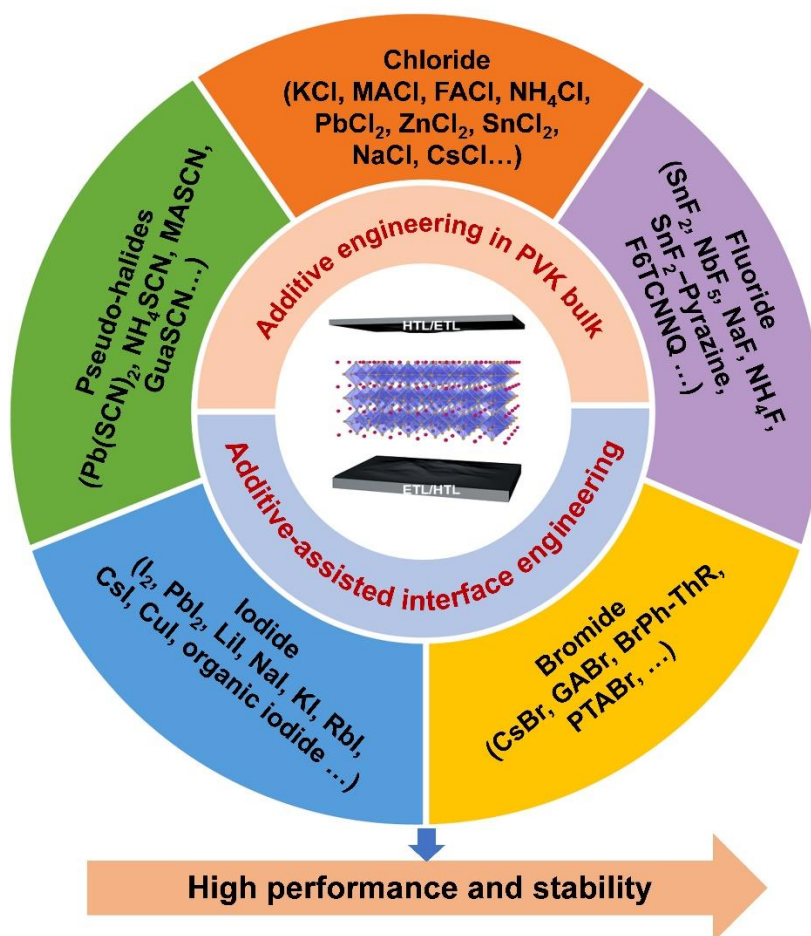
*[a] F. Cheng and Prof. T. Pauporté*

*Chimie ParisTech, PSL Research University, CNRS, Institut de Recherche de Chimie Paris (IRCP), UMR8247, 11 rue P. et M. Curie, F-75005 Paris, France.*

*E-mail : [thierry.pauporte@chimieparistech.psl.eu](mailto:thierry.pauporte@chimieparistech.psl.eu);*

*[www.pauportegroup.com](http://www.pauportegroup.com)*

*\*Authors for the correspondence*



## Abstract

Perovskite solar cells (PSCs) are attracting a tremendous attention from the scientific community due to their excellent power conversion efficiency, low cost and great promise for the future of solar energy. The best PSCs have already achieved a certified power conversion efficiency (PCE) of 25.5% after an unprecedented rapid performance rise. However, high requirement with respect to large area, high efficiency devices and stability are still the challenges. Major efforts, especially for achieving a high degree of chemical control, have been made to reach these targets. The use of halide additive has been playing a critical role in improving the efficiency and stability. The present paper reviews the important breakthroughs in PSC technologies made by using halide additives, especially chloride, and pseudo-halide additives for the preparation of the perovskite layers, other layers and interfaces of the devices. These additives help perovskite (PVK) crystallization and layer morphology control, grain boundary reduction, bulk and interface defects passivation and so on. Normally, these halide

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additives play different roles depending on their categories and their location. Herein, we review recent progresses made due to additives employment in every possible layer of PSCs. We develop chloride, other halides and pseudohalides as additives in PVK films, halide additives in carrier transport layers and at PVK-contact interfaces. Finally, an outlook of halide additive engineering in PSC progress is given.

**Keywords:** Perovskite solar cell; Halide additives; Chloride additives; Pseudo-Halide additives; High efficiency; High stability.

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## 1. Introduction

The use of halide perovskites (PVKs) in all solid-state solar cells appeared less than a decade ago and has revolutionized the field of photovoltaics (PV).<sup>[1-6]</sup> PVKs are highly flexible semiconductors with many advantages for this application such as high light absorption coefficient,<sup>[7]</sup> high charge carrier mobility,<sup>[8]</sup> long charge carrier diffusion length<sup>[9]</sup> and a bandgap tunable over a large energy range.<sup>[10]</sup> PVK thin films can be prepared from precursor solutions at mild temperature ( $\leq 160^\circ\text{C}$ ) on either insulating or conducting substrates.<sup>[11-14]</sup>

Perovskite solar cells (PSCs) can be considered as a competitor of silicon solar cells as well as a complementary technology in the case of multijunction solar cells.<sup>[15, 16]</sup> A typical hybrid metal halide PVK has a three-dimensional structure (3D) with a chemical formula of  $\text{ABX}_3$ , where A is an organic or inorganic cation, such as  $\text{FA}^+$  (formamidinium),  $\text{MA}^+$  (methylammonium) or  $\text{Cs}^+$  (cesium), B is a metal cation, such as  $\text{Pb}^{2+}$  or  $\text{Sn}^{2+}$ , and X is an halogen anion, such as  $\text{I}^-$  or  $\text{Br}^-$ .<sup>[17, 18]</sup> In PSCs, the PVK thin film is only several hundred nanometers thick and is contacted on both sides by semiconductor selective contact layers. An electron transporting layer (ETL) ensures the photogenerated electron collection and transport.<sup>[19, 20]</sup> While, on the other side, holes are collected and transported by a hole transporting layer (HTL).<sup>[21, 22]</sup> Depending on the position and structure of these layers, three different typical PSC architectures are distinguished : direct mesoporous, direct planar and inverted planar as schematically presented in Fig. 1A.<sup>[23]</sup> According to NREL, the certified power conversion efficiency (PCE) for a PVK cell achieves a present 25.5 % value,<sup>[24]</sup> which is superior to any other thin film technology and approaches the record for Si single crystal technologies. However, according to the recalculated Shockley-Queisser limit,<sup>[25, 26]</sup> for AM 1.5G ( $1000.4 \text{ W m}^{-2}$ ) and a temperature of 298.15 K, a highest theoretical PCE of 32.91% (short-circuit photocurrent density ( $J_{sc}$ ) =  $32.88 \text{ mA cm}^{-2}$ , open circuit voltage  $V_{oc}$  = 1.122 V, and fill factor ( $FF$ ) = 89.3%) can be expected for a single junction PSC with a bandgap ( $E_g$ ) of 1.4 eV. It indicates that PSC technology still presents space for performance improvement. Finding a light absorbing PVK material with the optimal  $E_g$ , improving the lifetime and diffusion length of carriers, as well as reducing the recombination due to traps states at the interfaces, grain boundaries and in the bulk are of utmost importance to maximize the performance of PSCs. Comparing the parameter of certified efficiency in 2019 by KRICT/MIT and in 2018 by ISCAS, the improvement of PCE from 23.3% to 25.2% is owed to the improvement of the fill factor,<sup>[27]</sup> which is mainly limited by the carriers transport times.<sup>[28]</sup> Huang et al.<sup>[29]</sup> reported that

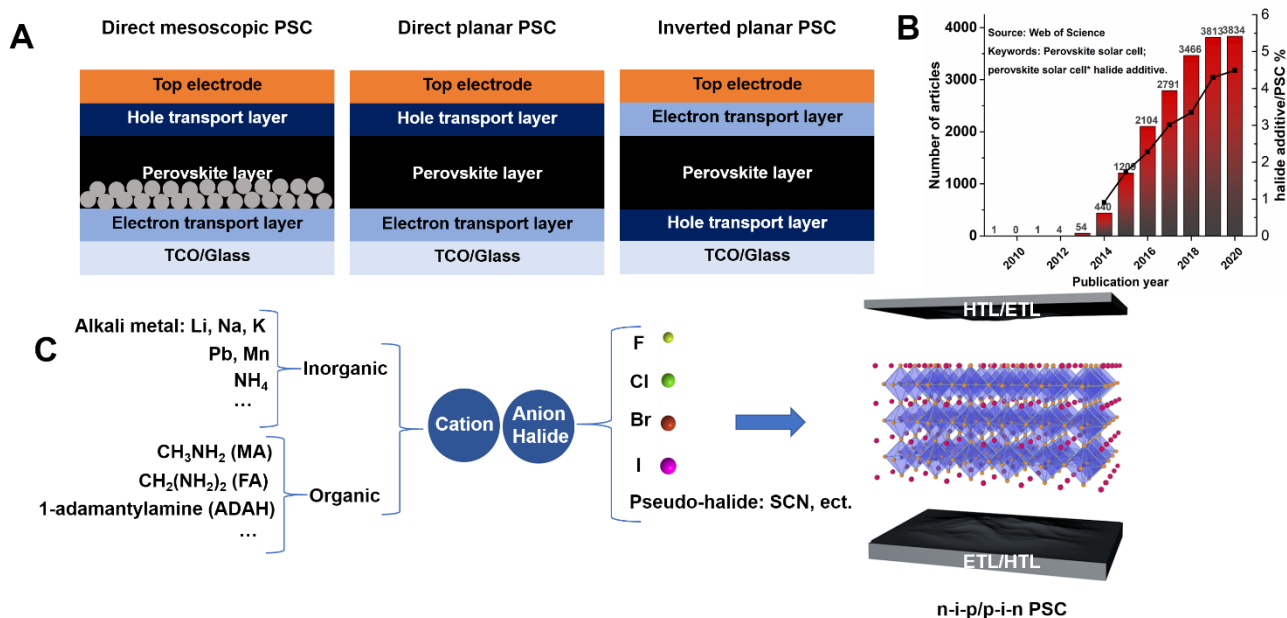
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FAPbI<sub>3</sub>-based PSCs could achieve an efficiency of 28.4 % with the trap density of thin film being reduced to its single crystal value. Besides, long-term stability is also a challenge for the commercialization and broad diffusion of PSCs.<sup>[30,31]</sup> Thus, much efforts have focused on fabricating highly oriented crystal films, increasing grain size, reducing traps, increasing heat, humidity, illumination stability and so on.<sup>[32-36]</sup> Among all the improvement methods, the employment of halide and pseudohalide additives for the preparation of various layers and treatments of interfaces is of major interest. The analysis of the web of science database reveals that the percentage of papers in which halide and pseudohalide additives are used in PSC is increasing (Fig. 1B). We can cite as recent examples You and co-workers<sup>[37]</sup> who got a certified PCE of 23.32% via a post-treatment by phenylethylammonium iodide (PEAI) and Kim and co-workers<sup>[38]</sup> who achieved a certified PCE of 23.48% using MAI as an additive and treating the PVK layer surface by PEA. More impressively, Seok et al.<sup>[39]</sup> got a PCE of 25.17 % and improved the device heat stability by relaxing the lattice strain of FAPbI<sub>3</sub> via cooperating methylenediamine dihydrochloride (MDACl<sub>2</sub>) and cesium iodide (CsI) into the PVK precursor.

These additives consist in salts composed of a large organic or inorganic cation combined to a halide anion: F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup> or a pseudo halide such as SCN<sup>-</sup> (Fig. 1C). These additives can be added into the PVK precursor solution, in the carrier transport material precursor solution or employed at the PVK-selective contact (ETL or HTL) interface. Finally, it is important to note that most of these additives will be fully or partly removed upon the post-annealing treatment of the layers. They will help the crystal to grow, the defect passivation, the stabilization of the structure, the improvement of interfaces and so on. Park et al.<sup>[40]</sup> comprehensively worked on the effect of different halide additives on FAPbI<sub>3</sub> films growth by introducing AX (A=FA, MA, Cs, Rb, NH<sub>4</sub>, X=Cl, Br, I) into PVK precursor, giving a sight of synergy effect of different halide species with FAPbI<sub>3</sub>. Liu et al.<sup>[41]</sup> compared the additives of PbCl<sub>2</sub>, PbBr<sub>2</sub> and MAI in MAPbI<sub>3</sub>. Researchers commonly focus on one or two kinds of halide additive in the specific PVK without a large view on the topic.<sup>[42-45]</sup> It thus appears important to review on how these varied halide additives cooperate with different PVK materials and different PVK solar cell layers in various PSC structures. In this perspective, we summarize the recent progresses on species of halide additives in halide PVK solar cells and their function such as the morphology adjusting, phase stabilizing, energy-level adjusting, trap state passivation and hysteresis elimination. A deep understanding of the relationship between halide/pseudohalide additive and the improved properties of PVK solar cell is presented. We have attached a special attention to the chloride and pseudohalide ones. First, in Section 2, we develop the employment of chloride additives for the preparation of PVK layers. Section 3 is dedicated to other halide and

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pseudohalide additives employed for PVK films synthesis. Section 4 reports on the use of halide additives in the carrier transport layers and interfaces of PSC. Finally, we provide a conclusion and an outlook of halide additive engineering in PSC progress.



**Fig. 1** (A) Schematic of the different PSC structures: direct mesoscopic, direct planar and inverted planar. (B) Halide additive research activities seen from the number of papers on PVK solar cell published each year. (C) Structure of this review, the additive species introduced into PSC.

## 2. Chloride additives for PVK films

A first breakthrough in PVK solar cell research field was achieved in 2012 with the first fabrication of all-solid-state devices.<sup>[46]</sup> At the early age of PSC science, the possibility of playing on non-stoichiometry and of using added halide compound in the precursor solution attracted the curiosity of scientists. Snaith et al.<sup>[47]</sup> combined an excess of methylammonium iodide (MAI) with a non-iodide lead source PbCl<sub>2</sub> in a 3:1 MAI:PbCl<sub>2</sub> molar ratio, to deposit high-quality films into mesoporous alumina. The PCE of 12.3 % was attributed to the efficient transport of carriers with minimal recombination losses in MAPbI<sub>3</sub>(Cl). Zhang et al.<sup>[48]</sup> latterly verified whether Cl or excess MA<sup>+</sup> was responsible for the enhanced diffusion length by fabricating a typical 1:1 PbI<sub>2</sub>:MAI and comparing it with the non-stoichiometric PbCl<sub>2</sub>:3MAI system. The higher optoelectronic property in the presence of PbCl<sub>2</sub> was explained by the easy removal of the MACl by-product upon the final annealing step at 100°C. They concluded that Cl is the key for high performance. Then after, a lot of research efforts



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focused on the employment of a large variety of either organic or inorganic chloride salts as additives to fabricate better performance PSCs. Most recently, Xu et al.<sup>[49]</sup> fabricated a two-terminal monolithic tandem cell with a triple-halide alloys PVK as top cell and achieved a PCE of 27% with an area of 1 square centimeter. Cl from MAPbCl<sub>3</sub> additive was detected throughout the film and was incorporated into the PVK lattice. Chloride, among all the halogens, is the most promising element for PSC performance improvement.

## 2.1 Inorganic chloride additives

In inorganic chloride additives, the cation includes alkali metal (K<sup>+</sup>, Na<sup>+</sup>, Li<sup>+</sup>),<sup>[50]</sup> Pb<sup>2+</sup>, Mn<sup>2+</sup><sup>[44]</sup> and ammonia species NH<sub>4</sub><sup>+</sup>.<sup>[50]</sup> Normally, inorganic chloride additives present in the PVK precursor solution increase the grain size as well as enhance the grain orientation and finally often increase the PCE of the device.

Following the pioneering research by Snaith et al. in 2012<sup>[51]</sup> and 2013<sup>[47]</sup>, the effects of metal chloride additives, especially PbCl<sub>2</sub>, were investigated in many further studies. Wang et al.<sup>[52]</sup> reported an improved PSC performance by incorporating PbCl<sub>2</sub> into the PVK precursor, forming a Lewis acid-base adduct. They showed that 2.5 mol% of PbCl<sub>2</sub> increases the grain size, charge carrier lifetime and electron-hole collection efficiency in MAPbI<sub>3</sub> PSCs. As a result, they achieved an average efficiency of 18.1 %. Cao et al.<sup>[53]</sup> studied the effect of PbCl<sub>2</sub> in a two-step method formation of MAPbI<sub>3</sub>(Cl), different concentrations of PbCl<sub>2</sub> (0%, 5 mol%, 10mol%) were introduced into PbI<sub>2</sub>/DMF solution. The mean grain size of MAPbI<sub>3</sub> increased from 223 nm to 353 nm when 5 mol% PbCl<sub>2</sub> was introduced. The diffraction peak intensity ratios of I<sub>(110)</sub>/I<sub>(310)</sub> and I<sub>(220)</sub>/I<sub>(310)</sub> were introduced to quantify the effects of chloride incorporation on grain orientation. The values of I<sub>(110)</sub>/I<sub>(310)</sub> and I<sub>(220)</sub>/I<sub>(310)</sub> increased to 15.13 and 6.49, respectively, when 5 mol% PbCl<sub>2</sub> was introduced, compared to 3.15 and 1.70 for the pristine film. It indicated a better preferred (110) grain orientation. The fast photoluminescence (PL) decay time and slow PL decay time of the 5 mol% PbCl<sub>2</sub> modified device were 0.43 ns and 40.81 ns, respectively (compared to the 3.47 ns and 39.08 ns without PbCl<sub>2</sub>). Finally, the device reached a maximum PCE of 17.05%.

The influence of alkali metal halides (KCl, NaCl, LiCl) as additives on the performance of PVK solar cells has been studied in a large extent. 0.75 wt.% KCl, 1 wt.% NaCl and 0.25 wt.% LiCl were introduced into PbI<sub>2</sub>/salt mixture.<sup>[54]</sup> The detailed parameters of the measured photovoltaic performances are gathered in Table 1. The best dosage for each alkali metal halide was given, among them, KCl at 0.75 wt.% got the best PCE. By x-ray diffraction (XRD) measurement, the average crystallite size was estimated using the Scherrer relationship:

$$D = 0.89\lambda/\beta \cos\theta \quad (1)$$

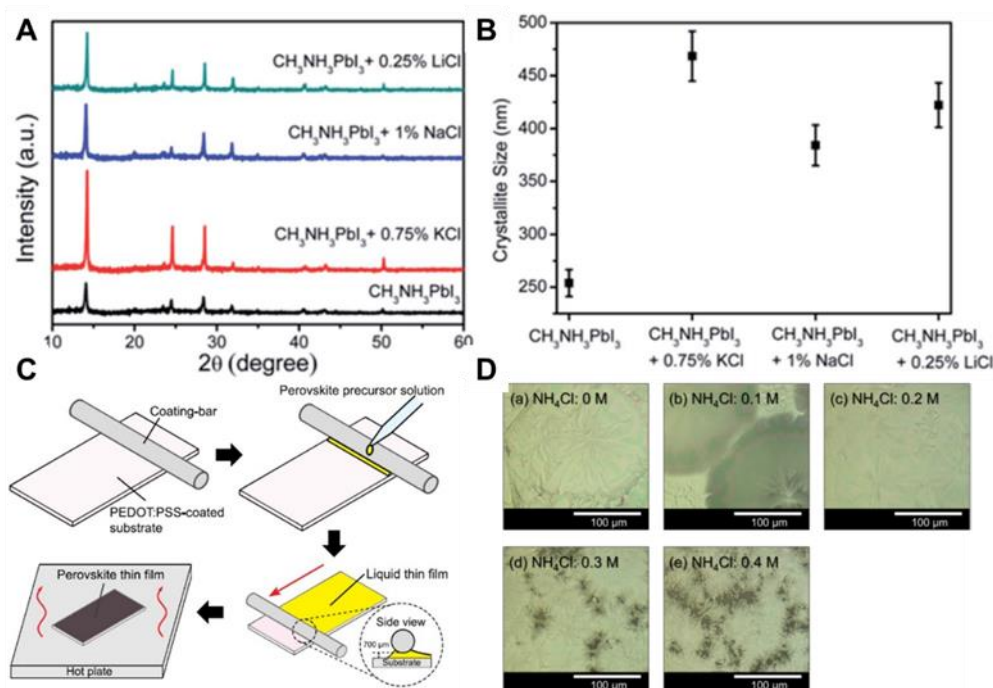
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$D$  is the crystallite size,  $\lambda$  is the wavelength of the X-rays,  $\beta$  is the full width at half maximum (FWHM) of the diffraction peak, and  $\theta$  is the diffraction angle. The crystallite sizes of the PVKs prepared with 0.75 wt.% KCl, 1 wt.% NaCl, and 0.25 wt.% LiCl were  $468 \pm 50$  nm,  $384 \pm 40$  nm, and  $422 \pm 40$  nm, respectively. The intensity of crystallinity and crystallite size (Fig. 2A, 2B) of the PVK film gave a glimpse of the reason why 0.75 wt.% of KCl got the best efficiency. Zheng et al. have clearly shown that  $K^+$  from KCl suppresses iodide mobility in PVK and linked it to  $J$ - $V$  curve hysteresis cancellation.<sup>[50]</sup>

**Table 1.** Photovoltaic performance parameters of devices prepared with various salt additives. (from Ref<sup>[54]</sup> with permission from The Royal Society of Chemistry, copyright 2013)

Salt	$V_{oc}$ (V)	$J_{sc}$ ( $\text{mA cm}^{-2}$ )	FF (%)	PCE (%)
0.75% KC	1.04	19.42	74.67	15.08 <sup>a</sup> (14.12) <sup>b</sup>
1% NaCl	0.96	17.59	75.62	12.77 <sup>a</sup> (12.14) <sup>b</sup>
0.25% LiCl	0.91	15.97	68.67	9.98 <sup>a</sup> (9.35) <sup>b</sup>
Without salt	0.9	15.88	76.31	11.4 <sup>a</sup> (10.86) <sup>b</sup>

<sup>a</sup> Best device performance. <sup>b</sup> Average performance from 10 devices.



**Fig. 2** (A) XRD patterns and (B) crystallite sizes in PVK thin films prepared without and with KCl, NaCl, and LiCl salt additives.<sup>[54]</sup> with permission from The Royal Society of Chemistry, copyright 2013; (C) Schematic

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*diagram of the fabrication process of PVK thin film by bar-coating; (D) Microscope images of MAPbI<sub>3</sub> thin films fabricated by bar-coating with various concentrations of NH<sub>4</sub>Cl.<sup>[55]</sup> with permission from Elsevier, copyright 2013.*

Fujii et al.<sup>[55]</sup> introduced NH<sub>4</sub>Cl additive into the MAPbI<sub>3</sub> precursor solution. By a bar-coating process (Fig. 2C) they obtained a highly (100)-oriented and uniform thin film of MAPbI<sub>3</sub> with large grains, giving a reference for industrial mass-production. As shown in Fig. 2D the homogeneous and large grains were obtained for 0.2 M NH<sub>4</sub>Cl additive. The solar cell utilizing the MAPbI<sub>3</sub> thin film prepared with 0.2 M NH<sub>4</sub>Cl demonstrated a hysteresis-free behavior and achieved a PCE of 12.5% with  $J_{sc}$  of 20.6 mA cm<sup>-2</sup>,  $V_{oc}$  of 0.83 V, and  $FF$  of 0.73 in the forward scan. Zong et al.<sup>[56]</sup> added NH<sub>4</sub>Cl with a molar ratio value of 0.8 to PbI<sub>2</sub> into the PVK precursor solution to adjust the kinetics of crystallization and growth of the active layer and it resulted in high-quality MAPbI<sub>3</sub> film formation. The diffraction peak intensity of the (110) face was enhanced and the FWHM reached a minimum value with an additive ratio of 0.8. It proved an increase of the crystallinity by NH<sub>4</sub>Cl. Combined with a hydrophobic carbon electrode, the final device got a PCE of 9.89% with a  $V_{oc}$  of 878.9 mV,  $J_{sc}$  of 22.38 mA cm<sup>-2</sup>,  $FF$  of 0.503. Under the condition of ambient air, the PSCs maintained 96% of the initial efficiency after 576 h due to the triple mesoporous scaffold<sup>[36]</sup> and PVK material quality. Pauporté et al.<sup>[50]</sup> demonstrated the benefit of employing NH<sub>4</sub>Cl additive combined with KCl for the preparation of methylammonium-free bromide-free Cs<sub>0.1</sub>FA<sub>0.9</sub>PbI<sub>3</sub> perovskite layers. They showed that KCl favors the PbI<sub>2</sub> precursor solubilization and it resulted in pure perovskite phase. The crystal growth speed and direction were controlled by NH<sub>4</sub>Cl which led to the formation of large crystal grains and well-crystallized layers. These authors used the glow-discharge optical emission spectroscopy (GD-OES) technique to directly visualize that potassium incorporated in the whole film blocks the iodide mobility by defect passivation. They clearly correlated the reduction (or suppression) of iodide mobility and the reduction (or suppression) of the  $J$ - $V$  curve hysteresis. Combined with the PVK surface treatment with n-propylammonium iodide (PAI), the cells reached at stabilized PCE of 21.1 %.

## 2.2 Organic chlorides additives

Organic chloride additives include a bigger-size cation, such as MA<sup>+</sup>, FA<sup>+</sup> or 1-adamantylamine (ADAH), compared to inorganic ones. Due to the bulky size of the organic cation, the interionic space is large, thus, the

attractive electrostatic force is weaker. Because chloride ion is volatile, it results in an easy removal of the organic chloride additive during the PVK annealing post-treatment.

Choy et al.<sup>[58]</sup> proposed that Cl<sup>-</sup> additive can significantly increase the hole and electron diffusion lengths, in agreement with the previously mentioned research by Snaith<sup>[47]</sup> in 2013. It also reduces the bulk trap-state density in PVK thin film. To investigate the role of chloride in different PSC devices architectures and thus provide a deeper understanding of its action mechanism, Burda et al.<sup>[59]</sup> prepared varied ratios of MACl : MAI (0:1, 0.5:1, 1:1, and 2:1) PVK film on planar and mesoporous TiO<sub>2</sub>/FTO substrates. They found by time-resolved photoluminescence (TRPL) spectroscopy (Table 2) that the interfacial electron injection rate from PVK to planar TiO<sub>2</sub> is accelerated with increasing Cl<sup>-</sup> content. It explained the increased PCE in direct planar device using Cl<sup>-</sup> as modifier. In contrast, Cl<sup>-</sup> demonstrated no influence on electron injection into mesoporous TiO<sub>2</sub>, suggesting that a reduction of interfacial charge recombination gives rise to the improved performance.

**Table 2.** Grain size, PL wavelength ( $\lambda_{PL}$ ), PL FWHM, PL decay lifetimes ( $\tau_{PL}$ ), PL rate constants ( $k_{PL}$ ), injection rate constants ( $k_{inj}$ ), injection efficiencies ( $\Phi_{inj}$ ), and PCEs ( $\eta_f$ ) of PVK films on planar or mesoporous TiO<sub>2</sub> coated FTO substrates.<sup>[59]</sup> With permission from The Royal Society of Chemistry, copyright 2018.

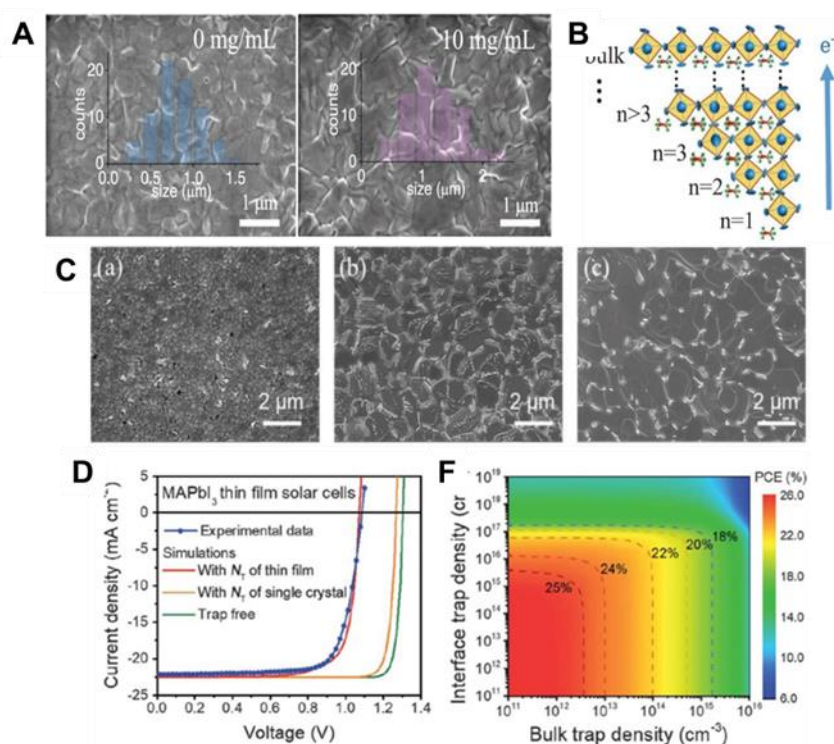
Architecture	Sample	Grain size (nm)	$\lambda_{PL}$ (nm)	FWHM (nm)	$\tau_{PL}$ ( $\pm 0.19$ ns)	$k_{PL}$ (s <sup>-1</sup> )	$k_{inj}$ (s <sup>-1</sup> )	$\phi_{inj}$ (%)	$\eta_f^a$ (%)
	x MACl for 1 MAI								
Planar	0 MACl	28	775	52	2.68	$3.7 \times 10^8$	$2.1 \times 10^8$	52	1.34
	0.5 MACl	39	778	49	2.27	$4.4 \times 10^8$	$2.7 \times 10^8$	59	9.5
	1 MACl	42	786	41	1.77	$5.6 \times 10^8$	$4.0 \times 10^8$	68	10.51
	2 MACl	46	784	47	0.98	$1.0 \times 10^9$	$8.5 \times 10^8$	83	10.85
Mesoporous	0 MACl	36	765	41	1.4	$7.1 \times 10^8$	$5.5 \times 10^8$	75	7.64
	0.5 MACl	22	754	54	1.05	$9.5 \times 10^8$	$7.9 \times 10^8$	81	9.12
	1 MACl	27	757	54	1.07	$9.3 \times 10^8$	$7.7 \times 10^8$	81	9.57
	2MACl	36	766	57	1.18	$8.5 \times 10^8$	$6.8 \times 10^8$	79	10.09

<sup>a</sup> From ref.<sup>[60-63]</sup>

2D PVKs are a class of two-dimensional quantum wells (QWs) compounds which include Dion-Jacobson (DJ) and Russlesden-Popper (RP) phases.<sup>[60-63]</sup> By incorporating 10 mg mL<sup>-1</sup> MACl into (GA)(MA)<sub>n</sub>Pb<sub>n</sub>I<sub>3n+1</sub> (GA=guanidinium; n=3) DJ film precursor solution, Luo et al.<sup>[40]</sup> got a champion stabilized PCE of 18.36% (with a stable  $J_{sc}$  of 20.86 mA.cm<sup>-2</sup>). In Luo's work, the grain size increased from  $\approx 0.3$ – $1.0$   $\mu\text{m}$  up to  $>3$   $\mu\text{m}$  as shown in Fig. 3A, and then grain boundaries were reduced. FWHM decreased from 0.165° to 0.143°, indicating an increased crystallite size. The emission peak position of the bulk phase varied from 760 to 754 nm in the PL measurement, the blueshift was attributed to a trap density reduction, yielding lower nonradiative recombination

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losses. The average lifetimes increased to 94.0 ns in TRPL measurements. The influence of additive concentration on the thickness distribution of QWs was also evaluated by femtosecond transient absorption (TA) spectroscopy. The additive enabled the formation of low- $n$  QWs and a narrower thickness distribution of high- $n$  QWs, leading to a gradient distribution of QW thickness. The carrier-populating time significantly decreased to 0.6–0.8 ps from 30 ps with the addition of 10 mg mL<sup>-1</sup> MACl, indicating that the additive enabled highly efficient electron transfer from low- $n$  QWs to the bulk phase due to an optimized thickness distribution of the QWs (Fig. 3B), which is beneficial for charge transport/extraction in solar cells. Finally, the optimized solar cells without encapsulation had much better environmental stability, thermal stability, and illumination stability.



**Fig. 3** (A) Top-view scanning electron microscopy (SEM) images and statistical chart of grain size of the 2D (GA)(MA)<sub>3</sub>Pb<sub>3</sub>I<sub>10</sub> films without and with 10 mg mL<sup>-1</sup> MACl additive. (B) Schematic thickness distribution of QWs and electron transfer from low- $n$  to high- $n$  QWs.<sup>[64]</sup> with permission from Wiley-VCH, copyright 2019. (C) Effect of MACl and CNT-NH<sub>2</sub> additives on the morphologies of MA<sub>0.85</sub>FA<sub>0.15</sub>PbI<sub>3</sub> thin films. SEM images of a) MA<sub>0.85</sub>FA<sub>0.15</sub>PbI<sub>3</sub>, b) MA<sub>0.85</sub>FA<sub>0.15</sub>PbI<sub>3</sub> (MACl), and c) MA<sub>0.85</sub>FA<sub>0.15</sub>PbI<sub>3</sub> (MACl)/CNT-NH<sub>2</sub> thin films.<sup>[65]</sup> with permission from Wiley-VCH, copyright 2019. (D) Measured and simulated  $J$ - $V$  curves of planar-structured solar cells based on MAPbI<sub>3</sub> polycrystalline thin films. The thin-film (single crystal) bulk and interface trap densities were adopted for the simulations. (E) Dependence of the PCE on MAPbI<sub>3</sub> thin-film bulk and interface trap densities. The dashed lines denote the contour lines of iso-PCE values.<sup>[29]</sup> With permission from the American Association for the Advancement of Science, copyright 2020



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In the work by Zhao et al.,<sup>[65]</sup> 0.05 mg mL<sup>-1</sup> of amino-functionalized carbon nanotube (CNT-NH<sub>2</sub>) and 0.21 M of MACl were employed to fabricate highly crystalline uniaxial-orientated PVK thin films with enhanced charge carrier transport. The MA<sub>0.85</sub>FA<sub>0.15</sub>PbI<sub>3</sub> (MACl) film showed enhanced crystallinity by XRD, and the peak intensity ratios of (110)/(310) and (220)/(310) became larger. It proved a preferred growth along the (110) and (220) crystallographic planes. The morphologies of modified film are shown in Fig. 3C. The average grain size reached > 1.5 μm by addition of MACl which was further enlarged to 2 μm with CNT-NH<sub>2</sub>. The champion PSC device (FTO/c-TiO<sub>2</sub>/SnO<sub>2</sub>/PVK/Spiro-OMeTAD/Ag) achieved a PCE of 21.05% with a  $J_{sc}$  of 23.52 mA cm<sup>-2</sup>,  $V_{oc}$  of 1.091 V, and  $FF$  of 0.82. The long-lasting charge carriers' lifetime in MA<sub>0.85</sub>FA<sub>0.15</sub>PbI<sub>3</sub> (MACl) films improved from 6.28 ns to 18.85 ns, compared with MA<sub>0.85</sub>FA<sub>0.15</sub>PbI<sub>3</sub>, but decreased to 4.78 ns with CNT-NH<sub>2</sub>. Such a decrease of PL lifetime is similar to the case of PVK films covered with charge transport (carrier- quencher) layers and indicated a promotion of charge-carrier transport by CNT-NH<sub>2</sub>.

Normally, the defects at the film surface and grain boundaries of PVK cause deep traps. These traps act as recombination centers for charge carriers. Ni et al.<sup>[29]</sup> studied the spatial and energetic distributions of trap states in halide PSC by Drive-level capacitance profiling (DLCP) method. They calculated that the trap density of the interfaces of polycrystalline PVK ranges between  $9.0 \times 10^{15}$  cm<sup>-3</sup> and  $2.0 \times 10^{17}$  cm<sup>-3</sup>, which is 1 ~ 2 orders of magnitude the bulk value. For the polycrystalline MAPbI<sub>3</sub> fabricated solar cell discussed in their work, the authors calculated that decreasing the interface trap density from  $1.0 \times 10^{17}$  cm<sup>-3</sup> to  $2.0 \times 10^{15}$  cm<sup>-3</sup>, would enhance the PCE to 25.4%, which is comparable to the PCE of 26.6% for trap-free MAPbI<sub>3</sub> thin film PVK solar cell (Fig. 3D and 3E).

Grätzel et al.<sup>[66]</sup> fabricated planar PSCs with SnO<sub>2</sub>/TiO<sub>2</sub> double layer oxide for an efficient electron extraction. They used MACl additive to aid the crystallization of the PVK film and get high quality large grains of PVK. The grain size enlarged to over 1 μm. Additionally, they treated the PVK film surface by iodine dissolved in isopropanol to passivate trap states. With Spiro-OMeTAD as HTL, the best PCE achieved 21.65% ( $J_{sc}$  of 23.2 mA cm<sup>-2</sup>, a  $V_{oc}$  of 1193 mV, and  $FF$  of 78.2%). By using PTAA as hole transporting material (HTM), the device maintained 96%, 90%, and 85% of their initial PCE values after 500 h continuous light soaking at 20, 50, and 65 °C, respectively.

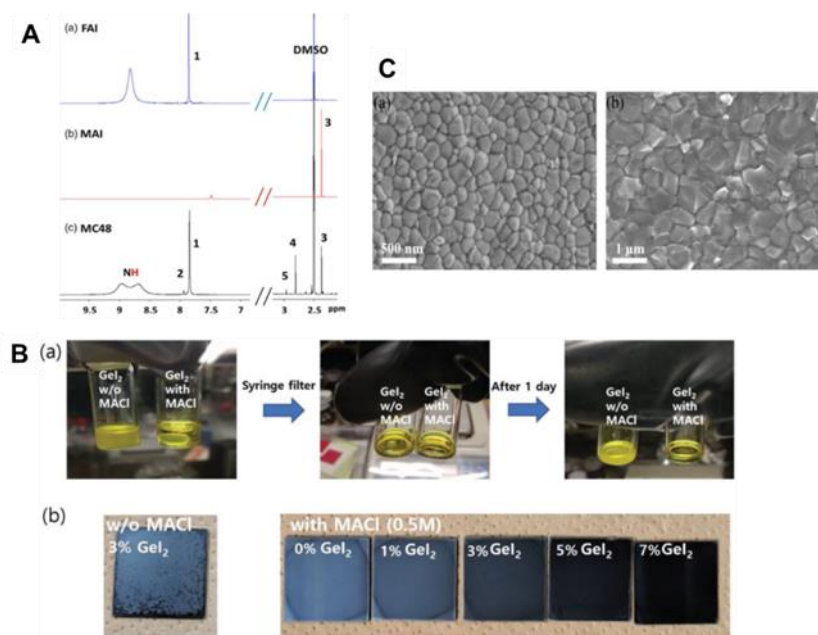
In a typical unstable PVK FAPbI<sub>3</sub>, the main function of MACl additive is to stabilize the black α-phase since it is easily transformed into yellow non-PVK δ-phase at ambient environment. Kim et al.<sup>[38]</sup> fabricated a high quality pure α-phase FAPbI<sub>3</sub> by employing 40 mol% of MACl as additive in the PVK precursor solution. The

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mechanism of MACl effect on the formation of  $\alpha$ -phase PVK was elucidated using DFT calculation. The formation energies revealed that Cl stabilizes the PVK structure thermodynamically. The projected density of states (PDOS) results revealed that Cl enhances the intensity of the p orbital of I at the HOMO state, then, the interactions of FA and I could be enhanced, thus improving the stability of FAPbI<sub>3</sub>. Attractively, the device got a PCE of 24.02% (23.48% for the certified one) with improved surface morphology, crystallographic properties, optical absorption, and PL properties.

One of us and co-workers employed methylammonium chloride (MACl) as additive at 20 to 55 mol% of PbI<sub>2</sub> precursor for the growth of FA<sub>1-x</sub>MA<sub>x</sub>PbI<sub>3</sub> PVK layers.<sup>[36, 67]</sup> The average grain size increased continuously with MACl with average values at 604 nm, 775 nm and 982 nm for 40 mol%, 48 mol% and 55 mol%, respectively. Monolithic PVK large grains were formed. Liquid-NMR was developed to analyze the photovoltaic layers. NMR peaks of MA, FA and of condensation products were identified and were reliably used to measure MA and FA content in films actually used in PSCs (Fig. 4A).  $x$  was quantified at  $0.06 \pm 0.01$  for the pure  $\alpha$ -phase films and was shown to correspond to the best entropic compound stabilization. The MACl excess was eliminated upon the annealing step. The best performance was achieved for 48 mol% MACl. It resulted in a stabilized PCE as high as 22.1%. These devices were also highly stable under solar irradiation and high moisture.

Kim et al.<sup>[68]</sup> found that the addition of MACl into PVK precursor solution not only improves the crystallinity, but also increases the solubility of GeI<sub>2</sub> (Fig. 4B). The 3% MACl-assisted Ge doped Pb-hybrid PVK film show superior PL lifetime of 18846 ns, a PCE of 22.7%, and a great stability toward illumination and humidity. 80% of the initial device performance was maintained after 1 month in 30~40% of relative humidity (RH).



**Fig. 4** (A) <sup>1</sup>H-NMR spectra of a) MAI, b) FAI, and c) FA<sub>0.94</sub>MA<sub>0.06</sub>PbI<sub>3</sub> layer with indexation. 1. NH=CHNH<sub>3</sub>I; 2. CH<sub>3</sub>NH<sub>2</sub>CH=NHI; 3. CH<sub>3</sub>NH<sub>3</sub>I; 4. CH<sub>3</sub>NH<sub>2</sub>CH=NHI þ CH<sub>3</sub>N=CHNH<sub>2</sub>CH<sub>3</sub>I; 5. CH<sub>3</sub>N=CHNH<sub>2</sub>CH<sub>3</sub>I (N,N'-dimethyl FAI).<sup>[36]</sup> with permission from Wiley-VCH, copyright 2020. (B) a) GeI<sub>2</sub>-containing DMF/DMSO organic–inorganic PVK (3% GeI<sub>2</sub>, FA<sub>0.83</sub>MA<sub>0.17</sub>Pb<sub>0.97</sub>Ge<sub>0.03</sub>(I<sub>0.9</sub>Br<sub>0.1</sub>)<sub>3</sub>) inks with and without MAI (0.5M). b) Pictures of PVK films of FA<sub>0.83</sub>MA<sub>0.17</sub>Ge<sub>x</sub>Pb<sub>1-x</sub>(I<sub>0.9</sub>Br<sub>0.1</sub>)<sub>3</sub> prepared without and with MAI additive and with various concentration of GeI<sub>2</sub> (x = 0-0.07).<sup>[68]</sup> with permission from Wiley-VCH, copyright 2020. (C) Top-view SEM images of PVK films a) reference and b) with the FAI additive.<sup>[69]</sup> with permission from Wiley-VCH, copyright 2021.

Formamidinium chloride (FACl) is another alternative for chloride source, with better solubility than MAI helping to get higher crystallinity. Suzuki et al.<sup>[70]</sup> mixed various mol% of FACl into the MAI and PbCl<sub>2</sub> precursor solution. Using 10 mol% of FACl additive, energy dispersive X-ray spectroscopy (EDX) mapping gave the molar ratio of Cl in the halogen component with the sum of I and Cl which was slightly increased to be about 7.5%. The performance with the photovoltaic PCE was improved from 9.59 % to 13.75% with  $J_{sc}$  of 22.5 mA cm<sup>-2</sup>,  $V_{oc}$  of 0.888 V,  $FF$  of 0.690. XRD patterns showed an increase of the (100) diffraction peak, a decrease of the FWHM and a peak shift due to a texturation of the layer, an increase of the crystal domain size and an enlargement of the d-spacing with addition of FACl at 10 mol%. Kong<sup>[69]</sup> modified PVK bulk with FACl while another Cl additive, 1-adamantylamine hydrochloride (ADAHCl, 3 mg.mL<sup>-1</sup> in chlorobenzene, CB) was employed for the surface treatment. It formed a high-density SAM and passivated the surface (Fig. 4C). A longer carrier lifetime at 22.3 ns and reduced carrier recombination were found. Based on the double Cl modification, a SnO<sub>2</sub>-based planar PSC was achieved with a PCE of 21.2%, low hysteresis, and high open circuit voltage of



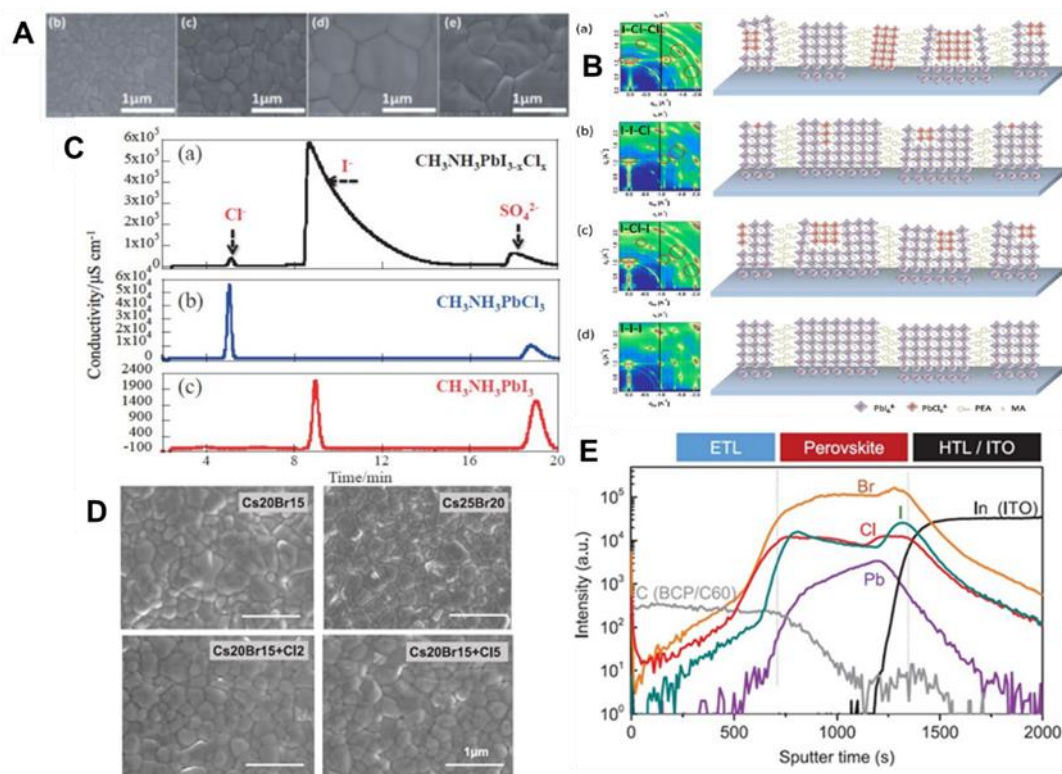
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1.152 V. 88% of initial PCE was retained after 700 h of aging under continuous illumination. Cl doping of MAPbI<sub>3</sub> is difficult to obtain due to the low formation energy and low boiling point of MAPbCl<sub>3</sub> at the origin of layer defects. A novel Cl containing additive, chloroformamidinium chloride (Cl-FACl)<sup>[71]</sup>, was presented as a “stabilizer” to restrain the removal of Cl avoiding the formation of defects in the layer. Gradually positive shift in XRD measurement indicated the shrinking of crystal lattice with the increase of smaller ions content doping, that is Cl and not Cl-FA. SEM showed that the grain size became larger with the concentration of Cl-FACl. The defects density based on the space charge limited current (SCLC) measurements and lifetime of TRPL decay measurements were calculated at  $4.75 \times 10^{15} \text{ cm}^{-3}$  and 110.1 ns, respectively, for the Cl-FACl doped PVK films. It was much lower and longer than that of without Cl-FACl ( $5.70 \times 10^{15} \text{ cm}^{-3}$  and 90.3 ns). For devices with 5 mol% Cl-FACl, a maximum PCE of 20.36% was achieved with lower hysteresis, 94% of their initial performance was retained after 600 minutes. Seok et al.<sup>[72]</sup> stabilized the  $\alpha$ -FAPbI<sub>3</sub> phase by doping with 3.8 mol% of methylenediammonium dichloride in replacement of MAPbBr<sub>3</sub> to get a methylammonium-free PSC. They achieved a certified PCEs of 23.7%. For the modified device, more than 90% of the initial efficiency was retained after 600 hours of operation at the maximum power point. Unencapsulated devices retained more than 90% of their initial PCE after annealing at 150°C in air for 20 hours.

### 2.3 Mechanism of chloride additives action on the growth of PVK films

Cl additives are mixed to the PVK precursor solution employed to prepare the films. Based on a coupled scanning transmission electron microscopy and energy-dispersive spectroscopy (STEM-EDS) measurements done by Dar et al.<sup>[73]</sup> in 2014, and a combined *in-situ* X-ray diffraction and *ex-situ* TOF-SIMS chemical analysis study done by Yang et al.<sup>[74]</sup> in 2016, Cl ions were proved to control the nucleation as well as the growth of MAPbI<sub>3</sub> without entering into the lattice. It rather resides at the grain boundaries after post-annealing because of its volatile property. Precisely, MACl controls the homogeneity of MAPbI<sub>3</sub> thin films by formation of intermediates with PbI<sub>2</sub> and reduction of the reaction rate between PbI<sub>2</sub> and MAI. The crystal growth rate is slowed-down and the crystals are more uniform. Consequently, the grains are larger, the film morphology is improved with less pinholes. It finally enhances the photovoltage property of the cell. To verify the function of MACl in the intermediate state, Dai et al.<sup>[75]</sup> demonstrated a novel facile intermediate engineering. They dripped 20 mg.mL<sup>-1</sup> MACl onto the deposited FAI-MAI-PbI<sub>2</sub>-DMSO intermediate film before the end of the second stage of spinning. They showed that this MACl treatment induces an ion exchange process in the FAI-MAI-

PbI<sub>2</sub>-DMSO intermediate phase and transforms it into FAI-MAI-MACl-PbI<sub>2</sub>-DMSO intermediate phase, further suppressing the crystal evolution rate and letting grains more time to evolve and self-embedding into the lattice network. As illustrated in Fig. 5A, 20 mg mL<sup>-1</sup> MACl modified film got a maximum grain size of 770 nm, and the lowest root-mean-square roughness of 11.6. Finally, the fabricated FTO/SnO<sub>2</sub>/PVK/spiro-OMeTAD/Au achieved a PCE of 20.4%.



**Fig. 5** (A) Surface SEM images of the films prepared with varied concentrations of MACl, (b) control film without-treatment, and films treated with c) MACl-10, d) MACl-20, e) MACl-30.<sup>[75]</sup> with permission from the American Chemical Society, copyright 2020. (B) GIWAXS images and proposed crystal orientation for a) I-Cl-Cl, b) I-I-Cl, c) I-Cl-I and d) I-I-I LDRP PVK films. The characteristic peaks in chloride-containing systems are shown in red rings.<sup>[76]</sup> with permission from Elsevier, copyright 2019 (C) Ion chromatography analysis of three different PVK solutions a) CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub>, b) CH<sub>3</sub>NH<sub>3</sub>PbCl<sub>3</sub>, and c) CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>.<sup>[77]</sup> With permission from the The Chemical Society of Japan, copyright 2015 (D) Top-view SEM images showing no evident difference in apparent grain size between triple-halide PVKs and double-halide control films; (E) TOF-SIMS depth profiles show the uniform distribution of halides throughout the entire film thickness of the triple-halide PVK (Cs<sub>20</sub>Br<sub>15</sub>+Cl<sub>5</sub>).<sup>[49]</sup> With permission from the American Association for the Advancement of Science, copyright 2020

The mechanism of optical and electronic properties improvement by Cl for low dimensional Ruddlesden-Popper (LD-RP) PVKs solar cell was also investigated. Devices with PbI<sub>2</sub>+PEACl+MAI (I-Cl-I), PbI<sub>2</sub>+PEAI+MACl (I-I-Cl), PbI<sub>2</sub>+PEAI+MAI (I-I-I), PbI<sub>2</sub>+PEACl+MACl (I-Cl-Cl) were fabricated.<sup>[76]</sup> It was

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confirmed by XRD that a part component of chloride generated the  $(\text{PEA})_2\text{MA}_{n-1}\text{Pb}_n\text{Cl}_{3n+1}$  ( $\text{PbCl}_6^{4-}$ ) phase. Grazing-incidence wide-angle X-ray scattering (GIWAXS Fig. 5B) technique was used to understand the effect of Cl position on crystallinity of the film. Results proved that Cl on PEA prefers to form  $\text{PbCl}_6^{4-}$  compared to that on MAI. PVK prepared from mixed Cl and I precursor demonstrated a longer charge carrier lifetime (668.15 ns) and diffusion length. SEM results showed that the incorporation of chloride significantly improved the PVK morphology with increased grain size, enhanced crystallinity, and uniform and smooth surface. Finally, a best PCE of 12.78% was achieved for the I-I-Cl system in a ITO/PEDOT:PSS/PVK/PCBM/LiF/Al solar cell structure.

The role of Cl on the PVK synthesis mechanism can be explained by the formation of intermediate species that favor the growth and crystallization of the final compound. It results in improved carrier lifetime and diffusion length, defect passivation and a phase stabilization which are of great profit for the final performance.

## 2.4 Measurement of the residual chloride in the layers

We have seen that many studies have reported the application of chloride additives in PVK precursor solution to optimize the morphology and surface passivation but with little or no chloride incorporation into the bulk material. It is commonly known that  $\text{Cl}^-$  volatilizes (evaporates) during annealing of the PVK film but could also reside at the grain boundaries or on PVK film surface. Chloride compounds mainly act as film crystallization controllers or play a role in the passivation of the PVK-contact interface. The content of probably residual Cl in the bulk were investigated by EDS, XPS, XRD and so on.  $\text{Cl}^-$  content is always below the detection limit of these techniques. For instance, Pauporté et al.<sup>[36, 67]</sup> could not detect a quantifiable amount of Cl by EDX in  $\text{FA}_{1-x}\text{MA}_x\text{PbI}_3$  layers prepared with precursor solutions containing 48 mol% of MAI with respect to  $\text{PbI}_2$ .

Moreover, the lattice parameters determined by XRD are easily influenced by other factors such as mechanical stress. Therefore, some researchers claimed that  $\text{Cl}^-$  is removed without incorporation into the crystal lattice. However, the content of Cl residual could be measured in some cases, depending on the doping level, source of Cl, halogen balance in the perovskite precursor solution/initial stoichiometry, and measurement technique.

Mosca et al.<sup>[78]</sup> found in 2013 that low concentration of Cl incorporated in a iodide-based structure did not change the  $E_g$ , but improved the charge transport in the PVK layer. Devices with methyl ammonium lead iodide PVK (PS1) layer, methyl ammonium lead iodide chloride (PS2) layer (3:1 MAI:PbCl<sub>2</sub>) and lead halide mixture

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(PS3) layer (1:1MACl:PbI<sub>2</sub>) were fabricated. Their bandgap was  $1.60 \pm 0.01$  eV. PS1 was poorly crystal oriented, while PS2 had a high orientation. A 0.7% reduction of the unit cell volume with respect to PS1 proved Cl-doping in PS2. For PS3, a high orientation pointed out a further phase, cubic MAPbCl<sub>3</sub> ( $a = 5.683(2)$  Å). The segregation of the cubic MAPbCl<sub>3</sub>, besides the Cl-doped MAPbI<sub>3</sub> phase proved the low incorporation of Cl into I based PVK films. In 2015, Cojocaru et al.<sup>[77]</sup> were the first to calculate the exact content of Cl<sup>-</sup> in the final film by ion chromatography. CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>, CH<sub>3</sub>NH<sub>3</sub>PbCl<sub>3</sub>, and CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub> layers were dissolved in 0.15 M sulfuric acid and injected into an ion analyzer equipped with an anion-exchange column and a conductivity detector. Standard solutions of known concentration were used for I<sup>-</sup> and Cl<sup>-</sup> calibration. As shown in Fig. 5C, for the film prepared with PbCl<sub>2</sub> and CH<sub>3</sub>NH<sub>3</sub>I in a 1:3 molar ratio, they found a 0.06:2.94 molar ratio of Cl to I which is equivalent to 2%.

In the work by Xu et al.<sup>[49]</sup>, MAPbCl<sub>3</sub> was employed into FA<sub>0.75</sub>CS<sub>0.25</sub>Pb(I<sub>0.8</sub>Br<sub>0.2</sub>)<sub>3</sub> PVK. In contrast to prior reports that Cl additive increases the grain size by modifying the nucleation and crystal growth, enlargement of grain domains was not observed in this research (Fig. 5D). As shown by time-of-flight secondary ion mass spectrometry (TOF-SIMS) depth profiling (Fig. 5E), Cl was uniformly distributed throughout the film. Taken the EQE, XRD, SEM, XPS, and SIMS results together, it was concluded that Cl was incorporated into the PVK lattice and increased its  $E_g$ , rather than being eliminated in a volatile phase. In a further experiment, MACl was added alone into PVK, the band gap did not raise, in agreement with previous reports that MACl volatilize during the annealing process at the temperature from 100 °C to 140 °C.<sup>[67,79-81]</sup> By replacing some of the iodine by bromine to shrink the lattice parameter, the solubility of Cl was improved, and it resulted in a factor of 2 increase in photocarrier lifetime and charge-carrier mobility.

## 2.5 Other applications of chloride additives

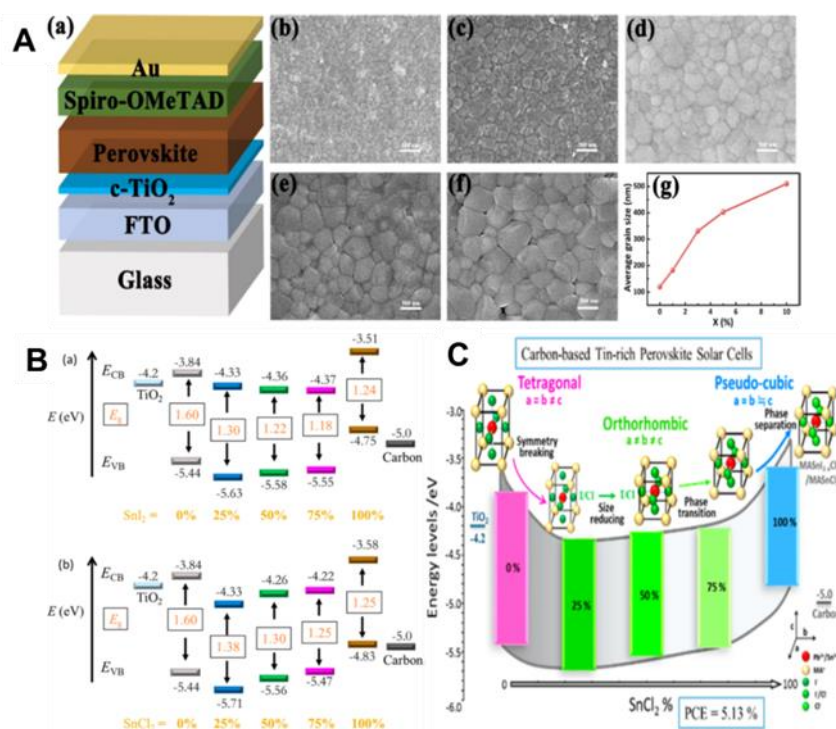
### 2.5.1 Fabricate lead-less PSC

Chloride additives have been employed with cations to partly replace Pb and thus fabricate more environmentally friendly PVK solar cells.<sup>[23]</sup> Jin et al.<sup>[82]</sup> replaced PbI<sub>2</sub> by 3% of ZnCl<sub>2</sub>. The modified device showed a great improvement in PCE from 16.4% to 18.2%, and the corresponding  $J_{sc}$ ,  $V_{oc}$ ,  $FF$  under reverse scan were 22.04 mA.cm<sup>-2</sup>, 1.09 V and 75.76 %. As illustrated in Fig. 6A, the grain size increased up to ~350 nm with 3% ZnCl<sub>2</sub> doping, without cracks nor pinholes. However, ZnI<sub>2</sub> doped film showed a similar increased

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crystal in grain size, confirming the crucial impact of Zn on the nucleation and crystal growth process. The FWHM of the (110) peak in XRD measurements decreased with increasing ZnCl<sub>2</sub>, indicating a better crystallinity, which is consistent with the SEM results. The film with 3% of ZnCl<sub>2</sub> showed the strongest intensity of PL and the maximum of 84.3 ns PL lifetime, which implies that ZnCl<sub>2</sub> doping reduces the traps and defects in the PVK layer. The MAI(PbI<sub>2</sub>)<sub>0.97</sub>(ZnCl<sub>2</sub>)<sub>0.03</sub>-based device had a 3% hysteresis index, much lower than the control device (10%). The recombination resistance (R<sub>rec</sub>) of electrical impedance spectroscopy (EIS) increased from 202.4 Ω to 910.9 Ω, indicating a decrease in recombination. The modified device degraded 7% of its initial PCE value after aging for 30 days in an ambient environment at 25–28 °C with 30–55% humidity without encapsulation.

Tsai et al.<sup>[83]</sup> replaced PbI<sub>2</sub> by 75% of SnCl<sub>2</sub>. The device of FTO/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>/MASn<sub>y</sub>Pb<sub>1-y</sub>I<sub>3</sub>(Cl)/NiO/C structure had a best 5.13% PCE with further addition of 30 mol % SnF<sub>2</sub>. SnCl<sub>2</sub> modified the conduction band energy (E<sub>CB</sub>), the valence band energy (E<sub>VB</sub>) and lattice structure (0%, tetragonal structure; 25%, orthorhombic structure; 50% of which with a substantially smaller unit cell; 75%, pseudocubic structure.) of PVK (Fig. 6B and 6C). The device modified by SnCl<sub>2</sub> showed anomalous optical and optoelectronic properties compared to the SnI<sub>2</sub> control.



**Fig. 6** (A) a) Schematic device architecture of MAI(PbI<sub>2</sub>)<sub>1-x</sub>(ZnCl<sub>2</sub>)<sub>x</sub> PVK solar cells. b–f) SEM surface images of the MAI(PbI<sub>2</sub>)<sub>1-x</sub>(ZnCl<sub>2</sub>)<sub>x</sub> PVK film with different ZnCl<sub>2</sub> (x = 0, 1, 3, 5, and 10%) content. g) Average grain size of MAI(PbI<sub>2</sub>)<sub>1-x</sub>(ZnCl<sub>2</sub>)<sub>x</sub> PVK film vs x.<sup>[82]</sup> with permission from the American Chemical Society, copyright



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2017 (B) Potential energy diagrams (energies in eV with respect to vacuum) of a)  $\text{CH}_3\text{NH}_3\text{Sn}_y\text{Pb}_{1-y}\text{I}_3$  and b)  $\text{CH}_3\text{NH}_3\text{Sn}_y\text{Pb}_{1-y}\text{I}_3(\text{Cl})$  films with Sn/Pb ratios controlled with  $\text{SnI}_2/\text{PbI}_2$  and  $\text{SnCl}_2/\text{PbI}_2$  precursors, respectively, at varied concentrations as indicated. (C) The lattice structure of PVK modified by  $\text{SnCl}_2$  concentration.<sup>[83]</sup> with permission from the American Chemical Society, copyright 2016

## 2.5.2 Fabrication of 2D/3D dimensional PVKs.

Hybrid 2D/3D PVKs are gaining an increasing interest in the field of halide PSC, the 3D component acts as an active material, while its 2D part provides protection against environmental degrading agents.

Wu et al.<sup>[84]</sup> added dodecylammonium-chloride (DACl) into the precursor solution of  $\text{FA}_{1-x}\text{MA}_x\text{PbI}_3$ . On the XRD pattern, the 3D-PVK peaks shifted towards higher angles and three peaks below  $10^\circ$  were present, indicating the formation of 2D-PVK. SEM images of PVKs films with increasing concentration of DACl showed denser and larger jigsaw-like crystals oriented perpendicular to the substrates. The PL-lifetime was improved from 3.15 ns to 26 ns by lowering the dimensionality. Incorporation of 8% DACl into the film reduced the defect levels by 2D-PVK formation. The moisture stability test showed that PVK retained the absorption structural characteristics even after being exposed to a humid environment ( $\text{RH} > 50\%$ ) for more than 50 days. The best performance device exhibited a PCE of 5%, 82% of which was maintained after 6 days and 64% after 9 days in RH 50% and at a temperature of 85 °C.

Cl additive is also used in LED. It enables PVK blue-LEDs with narrowband and spectrally stable, without wavelength shift<sup>[85, 86]</sup> and it enhances the photoluminescence quantum efficiency.<sup>[86]</sup>

The list of the main chloride additives employed in PSC, cell structure, PCEs and  $J-V$  curve parameters are summarized in the Table 3.

In summary, the role of chloride on the PVK synthesis mechanism has been explained by the formation of intermediate species. They favor the growth and crystallization of the final compound. They endow PVKs with high crystallinity as well as enhanced the grain orientation and increased charge carrier lifetime, increased diffusion length and electron-hole collection efficiency. Chloride additives have been employed to passivate the charged defects of the surface and grain boundaries as well as to control of crystallization and formation of PVK films for attaining efficient and stable photovoltaics.  $\text{K}^+$  counter cation passivates trap states due to defects and blocks the iodide mobility. Many groups have investigated the possible mechanism of chloride additives engineered PVK crystallization process.  $\text{Cl}^-$  additives slows down the PVK formation rate to give uniform PVK film *via* forming the intermediate phase with  $\text{PbI}_2$  and reducing the reaction rate between  $\text{PbI}_2$  and MAI.

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However, just little or no chloride is incorporated into the bulk PVK: most Cl<sup>-</sup> evaporates during PVK annealing. Interestingly, Cl<sup>-</sup> additives can be used to stabilize the black  $\alpha$ -phase FAPbI<sub>3</sub>, because Cl<sup>-</sup> additive can enhance the intensity of the p orbital of I at the HOMO state and the interaction of FA and I. Finally, with synergy effect of other passivator, efficiency of 24.02% for (MA)FAPbI<sub>3</sub> PVK has been achieved.

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**Table 3.** Main chloride additives used in PVK, concentration, cell structure, PCE and J-V curve parameters.

Chloride additives in the precursor	Concentration/ PbI <sub>2</sub> <sup>a</sup>	Device structure	PCE (%)	J <sub>sc</sub> (mA.cm <sup>-2</sup> )	V <sub>oc</sub> (V)	FF (%)	Year <sup>Ref.</sup>
KCl	9 mol%	FTO/c-TiO <sub>2</sub> /mp-TiO <sub>2</sub> /Cs <sub>0.1</sub> FA <sub>0.9</sub> PbI <sub>3</sub> /PEAI/spiro-OMeTAD/Au	19.16	25.24	0.992	76.54	2021 <sup>[50]</sup>
KCl	0.75 mol%/ DMSO	ITO/PEDOT:PSS/MAPbI <sub>3</sub> /PC61BM/C60/BCP/Al	15.08	18.33	1.04	74.67	2016 <sup>[54]</sup>
KCl + NH <sub>4</sub> Cl	5 mol%, 30 mol%	FTO/c-TiO <sub>2</sub> /mp-TiO <sub>2</sub> /Cs <sub>0.1</sub> FA <sub>0.9</sub> PbI <sub>3</sub> /PEAI/spiro-OMeTAD/Au	20.05	25.21	1.012	78.61	2021 <sup>[50]</sup>
FACl	10 mol%	FTO/TiO <sub>2</sub> /MAPbI <sub>3-x</sub> Cl <sub>x</sub> /spiro-OMeTAD/Au	13.75	22.5	0.888	69.00	2019 <sup>[70]</sup>
FACl, ADAHCl	10 mg.mL <sup>-1</sup> ; 3 mg.mL <sup>-1</sup> (CB)	FTO/SnO <sub>2</sub> /(FAPbI <sub>3</sub> ) <sub>0.87</sub> (MAPbBr <sub>3</sub> ) <sub>0.13</sub> /spiro-OMeTAD/Au	21.20	23.4	1.152	78.30	2019 <sup>[71]</sup>
Cl-FACl	5 mol%	ITO/P <sub>3</sub> CT-N/MAPbI <sub>3-x</sub> Cl <sub>x</sub> /PC <sub>61</sub> BM/BCP/Ag	20.36	22.1	1.12	81.97	2019 <sup>[87]</sup>
PbCl <sub>2</sub>	2.50 mol%	FTO/TiO <sub>2</sub> /MAPbI <sub>3</sub> /spiro-OMeTAD/Au	18.10	23.5	1.04	75.00	2013 <sup>[52]</sup>
PbCl <sub>2</sub>	5 mol%	FTO/TiO <sub>2</sub> /MAPbI <sub>3</sub> /spiro-OMeTAD/Au	17.05	21.53	1.04	75.90	2019 <sup>[53]</sup>
DACl	8 vo%/PPS <sup>b</sup>	ITO/PEDOT:PSS/FAMAPbI <sub>3</sub> /PCBM/BCP/Ag	5	13.57	0.845	44.00	2019 <sup>[84]</sup>
NH <sub>4</sub> Cl	0.8 mol%	FTO/BL-TiO <sub>2</sub> /ML-TiO <sub>2</sub> /SL-ZrO <sub>2</sub> /MAPbI <sub>3</sub> /C	9.89	22.38	0.878	50.30	2019 <sup>[56]</sup>
NH <sub>4</sub> Cl	0.2 M	ITO/PEDOT:PSS/MAPbI <sub>3</sub> /PCBM/Ag	12.50	20.6	0.83	73.00	2020 <sup>[55]</sup>
NH <sub>4</sub> Cl	0.3 M	MgF <sub>2</sub> /Willow Glass/ITO/PTAA/MAPbI <sub>3</sub> /C60/BCP/Cu	19.72	22.83	1.092	79.10	2020 <sup>[88]</sup>
NH <sub>4</sub> Cl	30 mol%	FTO/c-TiO <sub>2</sub> /mp-TiO <sub>2</sub> /Cs <sub>0.1</sub> FA <sub>0.9</sub> PbI <sub>3</sub> /PEAI/spiro-OMeTAD/Au	19.34	25.32	1.004	76.08	2021 <sup>[50]</sup>
MACl	48 mol%	FTO/c-TiO <sub>2</sub> /mp-TiO <sub>2</sub> /FA <sub>0.94</sub> MA <sub>0.06</sub> PbI <sub>3</sub> /PEAI/spiro-OMeTAD/Au	22.18	25.94	1.06	80.62	2020 <sup>[67]</sup>
MACl	20 mol%	FTO/c-TiO <sub>2</sub> /MAPbI <sub>3</sub> /spiro-OMeTAD/Au	17.70	21.3	1.02	81.00	2019 <sup>[89]</sup>
MACl	15 mg.mL <sup>-1</sup>	FTO/TiO <sub>2</sub> /SnO <sub>2</sub> /(FAPbI <sub>3</sub> ) <sub>0.87</sub> (MAPbBr <sub>3</sub> ) <sub>0.13</sub> /spiro-OMeTAD/Au	21.65	23.2	1.193	78.20	2019 <sup>[66]</sup>
MACl	40 mol%	FTO/c-TiO <sub>2</sub> /mp-TiO <sub>2</sub> /FAPbI <sub>3</sub> /PEAI/spiro-OMeTAD/Au	24.02	25.92	1.13	82.00	2019 <sup>[38]</sup>
MACl	20 mg.mL <sup>-1</sup>	FTO/SnO <sub>2</sub> /FA <sub>x</sub> MA <sub>1-x</sub> PbI <sub>3</sub> /spiro-OMeTAD/Au	20.40	23.88	1.08	78.38	2020 <sup>[75]</sup>
MACl, CNT-NH <sub>2</sub>	0.21 M; 0.05 mg.mL <sup>-1</sup>	FTO/c-TiO <sub>2</sub> /SnO <sub>2</sub> /MA <sub>0.85</sub> FA <sub>0.15</sub> PbI <sub>3</sub> /Spiro-OMeTAD/Ag	21.05	23.52	1.091	82.00	2019 <sup>[65]</sup>
MACl	10 mg.mL <sup>-1</sup>	FTO/c-TiO <sub>2</sub> /(GA)(MA) <sub>n</sub> Pb <sub>n</sub> I <sub>3n+1</sub> (n = 3)/spiro-OMeTAD/Au	18.48	22.26	1.14	72.67	2019 <sup>[64]</sup>
MACl	0.5 M	FTO/TiO <sub>2</sub> /SnO <sub>2</sub> /FA <sub>0.87</sub> MA <sub>0.13</sub> (Ge <sub>0.03</sub> Pb <sub>0.97</sub> )(I <sub>0.9</sub> Br <sub>0.1</sub> ) <sub>3</sub> /spiro-OMeTAD/Au	22.70	24.67	1.18	78.00	2020 <sup>[68]</sup>
ZnCl <sub>2</sub>	3 mol%/ MAI	FTO/c-TiO <sub>2</sub> /MAI(PbI <sub>2</sub> ) <sub>1-x</sub> (ZnCl <sub>2</sub> ) <sub>x</sub> /spiro-OMeTAD/Au	18.20	22.04	1.09	75.76	2017 <sup>[82]</sup>



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SnCl <sub>2</sub>	75 mol% / MAI	FTO/TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /MASn <sub>y</sub> Pb <sub>1-y</sub> I <sub>3-x</sub> Cl <sub>x</sub> /NiO/C	5.13	19.63	0.457	57.20	2016 <sup>[83]</sup>
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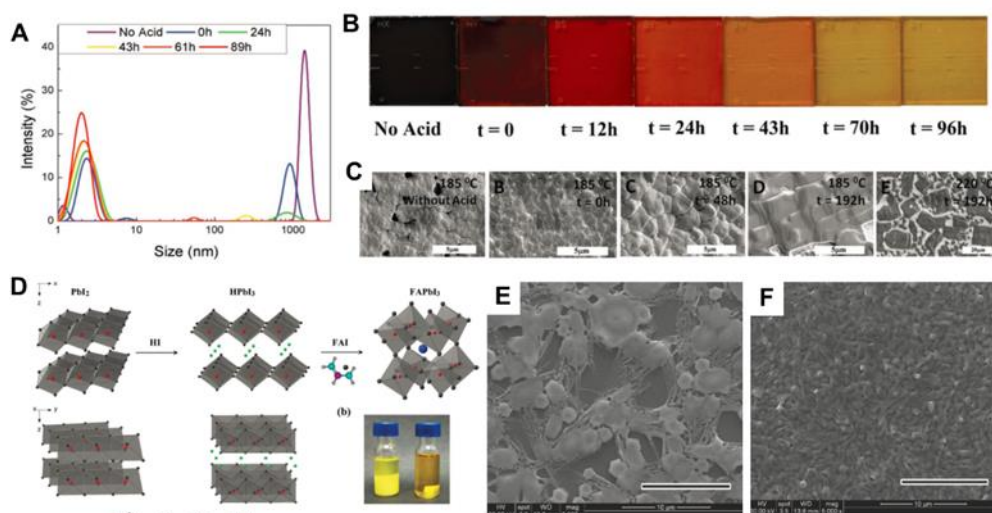
<sup>a</sup> Compared to PbI<sub>2</sub> precursor if not otherwise precised. <sup>b</sup> PPS : perovskite precursor solution.

### 3. Other halides and pseudo-halides additives for PVK films

#### 3.1 Halogen acids additives for PVK films

The PVK precursor solution is made of colloids of a lead polyhalide framework between organic and inorganic components.<sup>[17, 90]</sup> These colloids act as a nucleation center and determine the coverage and morphology of deposited thin films, especially large colloids induce a poor film morphology. Hydrohalic acids can dissolve large colloid particles and manipulate the colloidal concentration in the precursor solution, resulting in the modulation of the PVK morphology during the deposition process. Compared to neutral additives, the addition of acids can disrupt the interaction between solvent molecules and lower the solution viscosity, which, in turn, affects the solvent evaporation rate and determine the PVK crystallization rate.

Acids can improve the solubility of PVK precursors and help to obtain uniform and well-covering PVK films. In 2014, Eperon et al.<sup>[91]</sup> reported that the addition of HI helps to form uniform and continuous thin film. McMeekin et al.<sup>[92]</sup> investigated the nucleation and growth stages of PVK films by adding HI and HBr acids into  $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.2}\text{I}_{0.8})_3$  precursor solution. As shown in Fig. 7A, the colloids in suspension gradually dissolved, and the content of small colloidal particles increased with longer aging time after addition of acid. It critically impacted the crystallization kinetics and morphology of the thin films since colloids act as nucleation center (Fig. 7B, C). Finally, large grains and well-covering films were obtained by reducing the density of nucleation sites. However, a distinct trade-off between the grain sizes and pinhole density was observed. Since crystal growth also occurred in the vertical direction, the large crystal grains tended to be accompanied with undesirable pinholes. Heo et al.<sup>[93]</sup> deposited dense  $\text{MAPbBr}_3$  PVK films with well-surface coverage by adding HBr into  $\text{MAPbBr}_3$  precursor solution. The nucleation time of  $\text{MAPbBr}_3$  was retarded during spin-coating process due to the improved solubility of  $\text{MAPbBr}_3$  in DMF+HBr solution. A more-concentrated  $\text{MAPbBr}_3$  in DMF + HBr solution helped to yield thinner and better-covering PVK layers. It was noticed that the addition of the same amount of  $\text{H}_2\text{O}$  also enabled the formation of fully-covering  $\text{MAPbBr}_3$  layers, but the  $\text{H}_2\text{O}$  produced the decomposition of  $\text{MAPbBr}_3$  into  $\text{MABr}$  and  $\text{PbBr}_2$ .



**Fig. 7** Effect of acid additive on the colloid in the precursor solution. (A) Colloidal hydrodynamic size distribution of various PVK solutions. (B, C) Photographs and SEM views of thin films prepared with aged solution after the addition of Halogen acid.<sup>[92]</sup> with permission from Wiley-VCH, copyright 2017. (D) Schematic illustration of FAPbI<sub>3</sub> formation from PbI<sub>2</sub> with HI additive. (E, F) SEM images fabricated from FAI/PbI<sub>2</sub> and FAI/HPbI<sub>3</sub>, respectively.<sup>[94]</sup> with permission from Wiley-VCH, copyright 2015.

HI can react with PbI<sub>2</sub> to form HPbI<sub>3</sub> or HPbI<sub>x</sub>, which show better solubility than PbI<sub>2</sub> in DMF solution. Wang et al.<sup>[94]</sup> developed HPbI<sub>3</sub> to replace lead iodide and obtained highly uniform FAPbI<sub>3</sub> films (Fig. 7D). They proposed that the best performances of the HPbI<sub>3</sub> based PVK films may benefit from the slow crystallization process with exchange of H<sup>+</sup> and FA<sup>+</sup> ions in the PbI<sub>6</sub> framework (Fig. 7E and 7F). Pang et al.<sup>[95]</sup> demonstrated that the HPbI<sub>3</sub> can serve as precursor compounds to deposit uniform MAPbI<sub>3</sub> PVK film upon CH<sub>3</sub>NH<sub>2</sub> gas treatment. Upon exposed HPbI<sub>3</sub> into CH<sub>3</sub>NH<sub>2</sub> atmosphere, the CH<sub>3</sub>NH<sub>2</sub> molecules can react with H<sup>+</sup> to form CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>. After annealing, 1D HPbI<sub>3</sub> structure transformed into 3D MAPbI<sub>3</sub> PVK structure. H<sup>+</sup> plays a critical role in the formation of a stoichiometric, ultrasmooth and fully covering MAPbI<sub>3</sub> PVK thin films. Eperon et al.<sup>[96]</sup> first introduced HI additive into CsPbI<sub>3</sub> precursor solution, which made the conversion temperature from yellow to the black phase decreased to 100°C. It resulted in the formation of smooth and uniform black CsPbI<sub>3</sub> films. HPbI<sub>3</sub> was also employed to fabricate CsPbI<sub>3</sub> PSCs with improved stability and performance.<sup>[97]</sup>

In summary, halogen acid additives can modulate the morphology of PVK film via affecting the colloid particles and concentration in the precursor solution and reducing the crystallization rate. It results in better PVK morphology and trap states reduction.

### 3.2 Fluoride additives for PVK films

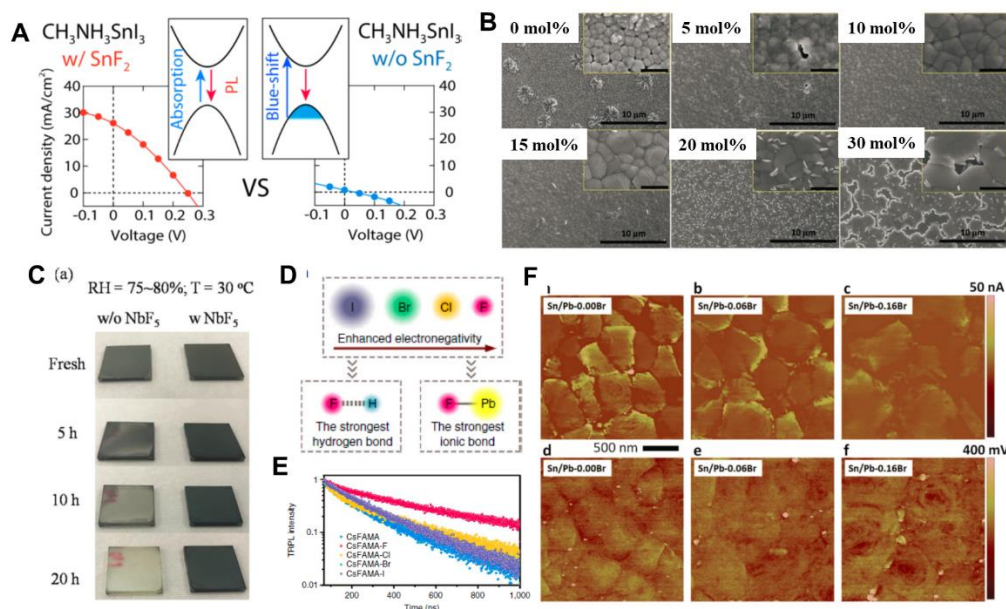
Due to the small size and large electronegativity of fluorine, fluoride species can form strong ionic and intermolecular bonding with PVK. Such strong chemical reactivity between fluoride and PVK is beneficial for passivating surface and crystal boundaries defects. Generally, when fluoride is incorporated into PVK film, it is typically present on the surface of PVK, exhibiting surface hydrophobicity and therefore protect the PVK from moisture erosion. Metal fluoride, such as SnF<sub>2</sub> and alkali fluoride, have been used in PSCs, especially, SnF<sub>2</sub> is employed in the tin halide PVK for suppressing the oxidation from Sn<sup>2+</sup> to Sn<sup>4+</sup>. Due to the toxicity of Pb which may limit the diffusion of the PSC technology, lead-free PVKs ASnX<sub>3</sub> have been intensively investigated. It is reported that MASnI<sub>3</sub> has a bandgap around 1.2 to 1.3 eV and an expected large short-circuit photocurrent. However, the PCEs of Sn-doped or entirely Sn-based PSCs are well-below that of Pb-based PSCs, and a large fraction of them is short-circuited. This mainly results from the oxidation of Sn<sup>2+</sup> to Sn<sup>4+</sup> in air and the intrinsic Sn-cation vacancies, as well as the poor morphology.

SnF<sub>2</sub> additive can suppress the oxidation of Sn<sup>2+</sup> to Sn<sup>4+</sup>. The tin-based PVK ASnX<sub>3</sub> are unintentionally hole-doped to a high degree, due to the Sn vacancies and the oxidation of Sn<sup>2+</sup>. Recently, SnF<sub>2</sub> additive in the lead-free PVK was shown to increase the Sn chemical potential and the formation energy of Sn vacancies, and then reduce the background carrier density and Sn defects.<sup>[98, 99]</sup> Handa et al.<sup>[100]</sup> reported a blue-shifted absorption edge for pure MASnI<sub>3</sub> thin film compared to the MASnI<sub>3</sub> with SnF<sub>2</sub> additive (Fig. 8A). It was assigned to the unintentional hole doping which induces a Burstein-Moss shift in the SnF<sub>2</sub>-free MASnI<sub>3</sub> samples. They demonstrated that SnF<sub>2</sub> additive reduces the hole density by about 1–2 orders of magnitude and suppresses the Sn<sup>4+</sup> formation. The PL lifetime of MASnI<sub>3</sub> with SnF<sub>2</sub> additive increased by one order of magnitude, resulting in improved performance of devices. For the effect of SnF<sub>2</sub> additive, Ma et al. proposed that SnF<sub>2</sub> just act as an inhibitor of Sn<sup>2+</sup> oxidation in the CH<sub>3</sub>NH<sub>3</sub>SnI<sub>3</sub> precursor solution for preparing undoped (Sn<sup>4+</sup>-free) film with lower defect concentration. Based on SEM images, XRD and UV-Vis spectra of CH<sub>3</sub>NH<sub>3</sub>SnI<sub>3</sub> film with 20 mol% SnF<sub>2</sub>, no SnF<sub>2</sub> or SnI<sub>2</sub> was found in the CH<sub>3</sub>NH<sub>3</sub>SnI<sub>3</sub> film.<sup>[101]</sup>

SnF<sub>2</sub> additive was used to modulate the crystallization process and improve the morphology of PVK films. F has a much smaller ionic radius (1.33 Å) than I (2.20 Å), therefore F doping of iodide PVK would not induce a significant variation in the lattice parameter and unwanted phases of film. Liao et al.<sup>[102]</sup> investigated the effect of SnF<sub>2</sub> additive on the morphology of FASnI<sub>3</sub> thin films. As shown in Fig. 8B, a flower-like structure with

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many pinholes was observed for the pure  $\text{FASnI}_3$  thin film. With increasing  $\text{SnF}_2$  concentration, the flower-like structures disappeared and the  $\text{FASnI}_3$  films became more uniform. It was noticed that a higher amount of  $\text{SnF}_2$  (>10%) induced severe phase segregation, resulting in obvious aggregates formation in the PVK film. As a result, the PCEs of Sn-based PSCs with optimized 10 mol%  $\text{SnF}_2$  additives increased to 6.22% in 2016. Lee et al.<sup>[103]</sup> selected  $\text{SnF}_2$ -pyrazine complex as additive in  $\text{FASnI}_3$  precursor solution to restrict the phase separation and reduce Sn vacancies formation. They also demonstrated the role of DMSO in forming a uniform PVK layer. During the spin-coating process, the crystallization of FAI and  $\text{SnI}_2$  was retarded by using DMSO as solvent, thereby producing a film with much better quality. Finally,  $\text{FASnI}_3$  PSCs with addition of  $\text{SnF}_2$ -pyrazine complex achieved a high PCE of 4.8%, and showed high reproducibility and stability for the encapsulated devices.



**Fig. 8** (A) Current–voltage curves of a  $\text{MASnI}_3$  solar cells (prepared with and without  $\text{SnF}_2$ ) recorded under AM 1.5G 1-sun irradiation.<sup>[100]</sup> with permission from the American Chemical Society, copyright 2020. (B) SEM images of  $\text{FASnI}_3$  PVK films with varying concentration of  $\text{SnF}_2$ , scale bar in all images are  $10\ \mu\text{m}$  and  $1\ \mu\text{m}$  (inset images).<sup>[102]</sup> with permission from Wiley-VCH, copyright 2017. (C) Humidity stability of  $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbI}_3$  PVK films without and with  $\text{NbF}_5$ .<sup>[104]</sup> with permission from Wiley-VCH, copyright 2019. (D) Schematic illustration of hydrogen bond between halogen and MA/FA ions. (E) TRPL spectra for the  $(\text{Cs}_{0.05}\text{FA}_{0.54}\text{MA}_{0.41})\text{Pb}(\text{I}_{0.98}\text{Br}_{0.02})_3$  PVK film with different sodium halide additives.<sup>[105]</sup> with permission from Springer Nature, copyright 2019. (F) AFM and (d) KPFM images of  $(\text{FASnI}_3)_{0.6}(\text{MAPbI}_3)_{0.4-x}(\text{MAPbBr}_3)_x$  ( $x = 0, 0.06, 0.16$ ) PVK films.<sup>[106]</sup> with permission from Wiley-VCH, copyright 2018.

$\text{SnF}_2$  additive was used to improve the phase stability. The use of  $\text{Sn}^{2+}$  cation results in a lower bandgap of

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PVK compared to  $\text{Pb}^{2+}$ ,<sup>[107]</sup> while the phase transformation and facile oxidation of  $\text{Sn}^{2+}$  to  $\text{Sn}^{4+}$  lead to the instability and poor performance for the PSCs. It is known that the tolerance factors of the stable PVK materials  $\text{ABX}_3$  should lie between 0.78–1.05, where the tolerance factor is defined as:  $t = (R_A + R_X)/2(R_B + R_X)$  with  $R_A$ ,  $R_B$  and  $R_X$  the ionic radii of A, B and X ions, respectively. When F ion (as  $\text{SnF}_2$ ) is introduced stoichiometrically, into the  $\text{ASnI}_3$  PVK, forming a  $\text{ASnI}_{3-x}\text{F}_x$  PVK layer, the tolerance factor  $t$  becomes larger as  $x$  increases due to the smaller F ionic radius, and enhances the phase stability of Sn-based PVK. Therefore, fluoride complex was introduced as additive to improve the stability of Sn-based PVK. Wu et al.<sup>[108]</sup> demonstrated that F ion dopant inhibits the oxidation process, and slows down the phase transformation of  $\text{CsSnI}_3$  into  $\text{Cs}_2\text{SnI}_6$ .

Alkali fluoride is beneficial for reducing the positive and negative charged defects by forming chemical bonds with lead-based PVK. Yuan et al.<sup>[104]</sup> presented an efficient method to prevent the phase transformation from black  $\alpha$ -phase to yellow non-PVK  $\delta$ -phase by adding  $\text{NbF}_5$  material (Fig. 8C). The  $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbI}_3$  PVK film with  $\text{NbF}_5$  could maintain the black color without bleaching to transparent after 20 h, and the stability of PSC was much improved. The fluorine and niobium elements were distributed over the PVK surface, the strong Pb-F and Nb-I interactions between  $\text{NbF}_5$  and  $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbI}_3$  were probably the main reasons for the improved phase stability after  $\text{NbF}_5$  addition. Li et al.<sup>[105]</sup> explored an effective passivation of cation and anion vacancy defects via adding  $\text{NaF}$  into the triple-cation PVK ( $\text{Cs}_{0.05}\text{FA}_{0.54}\text{MA}_{0.41}$ ) $\text{Pb}(\text{I}_{0.98}\text{Br}_{0.02})_3$  layer. They compared the passivation effect of  $\text{NaX}$  ( $X=\text{Cl}, \text{Br}, \text{F}$ ) with tunable bond strength of halide with PVK layer (Fig. 8D). Although all sodium halides could improve the PVK quality, the fluoride-containing material gave the best results (Fig. 8E). Since the F ions can form hydrogen bonds ( $\text{N-H}\dots\text{F}$ ) with organic cations and ionic bonds with Pb at the PVKs surface, F ions are effective in passivating both the organic cations and halide vacancies. Meanwhile, the increased ionic bonding of PVK with fluoride ions also immobilized both organic cations and halide anions. Finally, the addition of  $\text{NaF}$  resulted in a best PCE of 21.46% in planar PSCs, and superb thermal and environmental stability for the PVK layer and devices.

### 3.3 Bromide additives for PVK films

The bandgap of organic halide PVK can be tuned by the  $p$ -orbital of halide, since the electronic structure of PVK is related to both halide and metal  $p$ -orbitals. Substitute iodide by bromide anion to create mixed-halide PVK can broaden the band gap of PVK film, generate longer lifetimes and improve stability.<sup>[109]</sup> The mixed-halide PVK films also exhibit enhanced stability toward ambient conditions.<sup>[110]</sup> Noh et al.<sup>[111]</sup> first tuned the



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bandgap of  $\text{MAPbX}_3$  from 1.6 eV to 2.2 eV covering almost the entire visible spectrum via adjusting the Br/I ratios. With this approach, Huang et al.<sup>[112]</sup> designed a novel prismatic PSC by connecting four  $\text{MAPbI}_x\text{Br}_{3-x}$  ( $x=3, 2, 1, 0$ ) subcells with different bandgaps in the same horizontal plane. Thermodynamic losses are mitigated by this approach and the incident high-to-low energy photons are harvested by horizontally aligned  $\text{MAPbI}_x\text{Br}_{3-x}$  subcells. As a result, the corresponding newly designed PSC generated a record  $V_{oc}$  of 5.3 V and PCE of 21.3%. The PVK with bandgap of 1.3-1.4 eV is pivotal for single junction PSCs because of the balance between absorption loss of sub-bandgap photons and thermalization loss of above-bandgap photons. Yang et al.<sup>[113]</sup> incorporated 20% Br into  $\text{MASn}_{0.5}\text{Pb}_{0.5}\text{I}_3$  to obtain an ideal bandgap (1.35 eV) absorber layer for single junction PSCs. This mixed-halide  $\text{MAPb}_{0.5}\text{Sn}_{0.5}(\text{I}_{0.8}\text{Br}_{0.2})_3$  PVK reduced the  $V_{oc}$  loss at 0.45 V and improved PCE to 17.63%.

Bromine incorporation can passivate grain boundaries. It is known that low- $E_g$  mixed Pb-Sn PSCs exhibits large  $V_{oc}$  deficits and low FF, because of the high dark saturation current density caused by high leakage current from grain boundaries.<sup>[114, 115]</sup> Li et al.<sup>[106]</sup> demonstrated that Br incorporation can passivate defects at grain boundaries and lower the dark saturation current density of low  $E_g$  mixed Sn-Pb PSCs. PVK films were prepared by spin-coating  $(\text{FASnI}_3)_{0.6}(\text{MAPbI}_3)_{0.4-x}(\text{MAPbBr}_3)_x$  ( $x = 0, 0.04, 0.06, 0.08, \text{ and } 0.16$ ) precursor solutions. In the fabrication process of annealing at 100 °C, the high temperature would drive Br out of PVK crystal lattice, resulting in higher Br concentration at grain boundaries than in grain bulk. Consequently, the grain boundaries contain a higher density of negatively charged defects than grain interiors confirmed by KPFM map (Fig. 8F). With Br additive, the mixed low- $E_g$  (1.272 V) Sn-Pb PSCs have achieved low  $V_{oc}$  deficits of 0.384 V, high FF of 75% and a PCE of >19%. Although mixed Sn-Pb PVK layer possesses ideal-bandgap for photovoltaic application, the best PCEs of Sn-Pb binary PSCs with <18% are lower than 1.5-1.6 eV bandgap pure-Pb-based PSCs with PCE of 24%.<sup>[116]</sup> The poor efficiency of Sn-Pb binary PSCs is attributed to the high defect density associated with  $\text{Sn}^{2+}$  oxidation, which leads to lower open circuit voltage (<0.9 V).<sup>[117]</sup> Therefore, some organic substances, such as  $\text{SnF}_2$ -Prazine,<sup>[103]</sup> guanidinium thiocyanate,<sup>[118]</sup> have been used as additive to reduce the high defect density caused by  $\text{Sn}^{2+}$  oxidation. Zhou et al.<sup>[119]</sup> discovered that guanidinium bromide (GABr) in the PVK film can passivate the defect related with  $\text{Sn}^{2+}$  oxidation, which improved the structural and photoelectric characteristics of Sn-Pb binary PVK  $(\text{FA}_{0.7}\text{MA}_{0.3}\text{Pb}_{0.7}\text{Sn}_{0.3}\text{I}_3)$  thin films. With optimized GABr concentration of 12%, Sn-Pb binary PVK films display increased grain size, decreased charge-carrier recombination, and reduced trap state densities, resulting in best PCE of 20.63% with a small  $V_{oc}$  deficit of 0.33 V.

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Lewis base usually act as electron donor, which can interact with positively charged under-coordinated  $\text{Pb}^{2+}$  ions. Organic Lewis base, such as thiophene, pyridine, thiourea etc, could efficiently passivate the under-coordinated  $\text{Pb}^{2+}$  and thus enhance the PCE and stability of PSCs. Zhang et al.<sup>[120]</sup> applied N-(4-bromophenyl)-thiourea (BrPh-ThR) as the Lewis base in the PVK solution precursor to investigate the cooperation passivation effect of organic cation and bromide. BrPh-ThR as an S-donor has a strong ability to coordinate with  $\text{PbI}_2$ , which is beneficial for the large grain PVK formation and defect passivation of the  $\text{Pb}^{2+}$  defects at crystal grain boundaries and surface. As a result, they obtained a 20.4% device efficiency with BrPh-ThR additive in precursor solution, compared with 19.3% for the control PSCs.

### 3.4 Iodide additives for PVK films

Recent studies show that the performance of PVK film could be improved through addition of solid iodine ( $\text{I}_2$ ), organic iodide,  $\text{PbI}_2$  and alkali metal iodides, LiI, NaI, KI, RbI and CsI. A complete understanding of these issues is important for obtaining high efficiency PSCs.

#### 3.4.1 Iodide ions additive

A large number of iodide additives have been employed in the literature to prepare 2D/3D PVK layers. The complete reporting of this research field is out of the scope of the present review and one can report on the recent review by Zhang et al.<sup>[121]</sup> to have an overview on the topic. The most successful approach developed up to now for getting highly stable PSCs has been to adopt a triple mesoscopic architecture where the HTL/metal back contact is replaced by a mesoporous carbon counter-electrode.<sup>[58, 122, 123]</sup> Such cells have recently successfully passed items of the IEC61215:2016 PV qualification test.<sup>[124]</sup> The employment of 5-Ammonium valeric acid iodide (5-AVAI) additive was shown important to facilitate the porous scaffold filling, to improve the contact with the oxide scaffold and to strengthen the  $\text{MAPbI}_3$  grain boundaries due to bifunctionality.<sup>[124]</sup> 4-(aminomethyl) benzoic acid hydroiodide additive has also been employed efficiently for the same purpose.<sup>[125]</sup> Yang et al.<sup>[126]</sup> reported a defect-engineering strategy with iodide management for fabricating formamidinium-lead-halide-based PVK. Solid iodine ( $\text{I}_2$ ) was dissolved in isopropanol (IPA) and formed to  $\text{I}_3^-$  ions, which was added into the dripping solution of FAI (+ MABr) for increasing the proportion of the crystalline  $\alpha$ -FAPbI<sub>3</sub> phase and reducing the concentration of defects in the entire PVK layer. The fabricated PSCs exhibited a

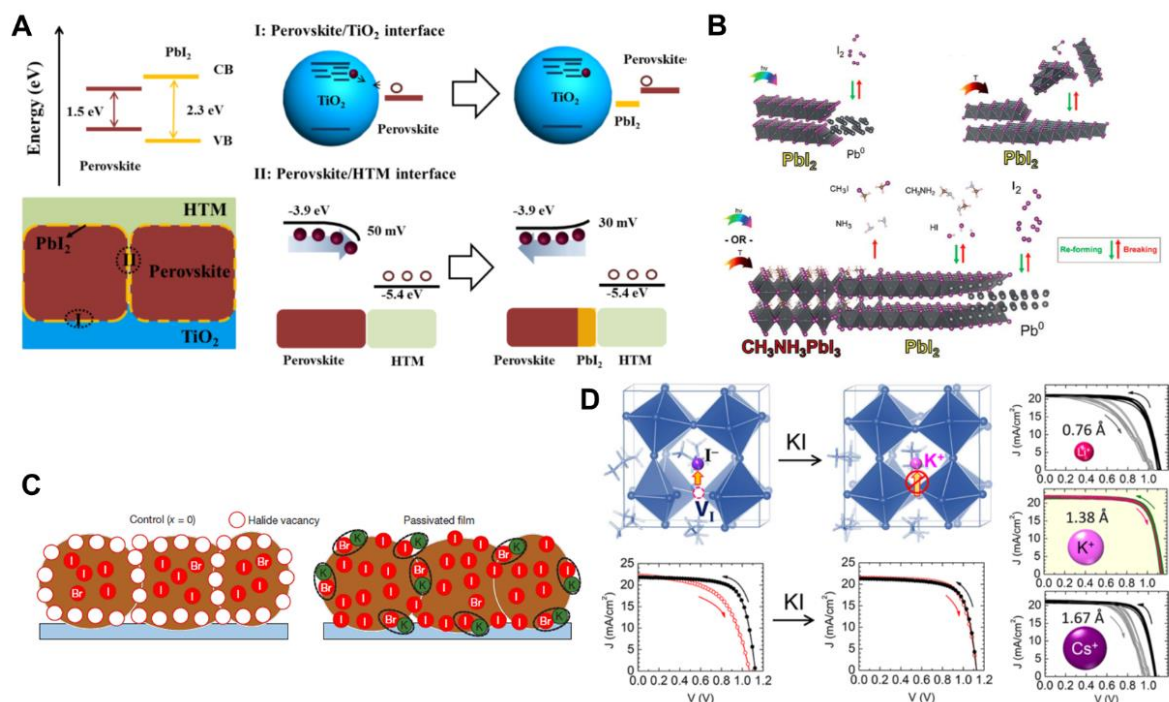


certified power conversion efficiency of 22.1% in small cells and 19.7% in 1-square-centimeter cells.

### 3.4.2 Excess amount of $\text{PbI}_2$ and other inorganic iodide additives

Although the precise stoichiometry of halide PVK precursor solution is important for making PVK film, a slight excess of  $\text{PbI}_2$  on the PVK grains is beneficial for the performances of PSCs.<sup>[127]</sup> The mechanism for the effect of  $\text{PbI}_2$  on the PSCs performances have been investigated. Lead iodide, a p-type semiconductor with a large bandgap of 2.3 eV,<sup>[128]</sup> could passivate and eliminate defect states due to a band edge matching between PVK,  $\text{PbI}_2$ , and the HTL.<sup>[129, 130]</sup> Zhang et al.<sup>[13]</sup> investigated the  $\text{MAPbI}_3$  could decomposed into  $\text{PbI}_2$  and organic species with annealing time excess. By releasing the organic species,  $\text{PbI}_2$  formed in PVK films could passivate and eliminate defect states and enhance the device performance. Chen et al.<sup>[130]</sup> demonstrated a self-induced passivation strategy of  $\text{PbI}_2$  for the  $\text{MAPbI}_3$  PVK to control the carrier injection and transfer behavior across the corresponding heterojunction. They discovered that the  $\text{MAPbI}_3$  would slightly decompose to  $\text{PbI}_2$  upon heating at 150 °C for more than 30 min. As shown in Fig. 9A,  $\text{PbI}_2$  excess can fill PVK grain boundaries, thereby reducing the number of trapping sites and form a favorable type I band alignment. This  $\text{PbI}_2$  passivator can reduce the carrier recombination at the interface of  $\text{TiO}_2/\text{PVK}$  and alleviate the barrier of charge extraction from PVK to HTL. The excess of  $\text{PbI}_2$  formed a passivating layer at the PVK gain boundaries and surface which induced to a longer recombination time, but too much  $\text{PbI}_2$  could act as an insulating layer and impair the device performance.<sup>[131]</sup> However, it is difficult to control the amount of  $\text{PbI}_2$  by such self-induced approach with annealing technique. Kim et al.<sup>[127]</sup> incorporated different amount of  $\text{PbI}_2$  into the PVK layers. They demonstrated that  $\text{PbI}_2$  excess in the PVK phases is highly beneficial for reducing the hysteresis of  $J$ - $V$  characteristics and ion migration. Finally, the best PSC fabricated using  $(\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}$  achieved a PCE of 20.1% with 5.7 mol%  $\text{PbI}_2$  excess incorporated. Zhang et al.<sup>[132]</sup> developed a novel approach to fabricate PVK passivated by a controllable  $\text{PbI}_2$  amount by using hydrohalide deficient  $\text{PbI}_2 \cdot x\text{HI}/\text{Br}$  ( $x < 1$ ) precursors reacted with  $\text{CH}_3\text{NH}_2$ . Both  $\text{MAPbI}_3$  and  $\text{MAPbI}_2\text{Br}$  PVK solar cells prepared via  $\text{MA}+(\text{PbI}_2+0.95\text{HI}/\text{Br})$  exhibited improved PV performance with a  $V_{oc}$  enhancement due to less charge recombination by  $\text{PbI}_2$  passivation. Moreover, authors have hypothesized that a small excess of  $\text{PbI}_2$  is beneficial for preparing larger PVK grains or improving their crystallinity, resulting in enhanced devices' performances.<sup>[131, 133, 134]</sup> Jiang et al.<sup>[134]</sup> investigated the synergistic effect of  $\text{PbI}_2$  passivation and Cl inclusion for improving the  $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$  PVK film growth and suppressing nonradiative recombination. It resulted in a record-high  $V_{oc}$  over 1.15V for

the  $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$  PSCs.



**Fig. 9** (A) Proposed mechanism for  $\text{PbI}_2$  passivation in  $\text{CH}_3\text{NH}_3\text{PbI}_3$  Film.<sup>[130]</sup> with permission from the American Chemical Society, copyright 2014. (B) The photodecomposition and thermal degradation processes of  $\text{PbI}_2$  and  $\text{MAPbI}_3$ .<sup>[135]</sup> with permission from The Royal Society of Chemistry, copyright 2018. (C) Schematic illustration of PVK film showing halide-vacancy management and the potassium passivation effect.<sup>[136]</sup> with permission from Springer Nature, copyright 2018. (D) Schematic view of  $\text{MAPbI}_3$  hybrid PVK structure with  $\text{I}$ -Frenkel defect, and the passivation effect of  $\text{KI}$  on the device performance.<sup>[137]</sup> with permission from the American Chemical Society, copyright 2018.

$\text{PbI}_2$  excess at the surfaces and grain boundaries of PVK films, due to a larger bandgap than PVK, results in electronic insulation and negative effect for the cell performance.<sup>[138, 139]</sup> Especially, a small excess amount of  $\text{PbI}_2$  has a detrimental effect on the stability of PVK.<sup>[140]</sup> As shown in Fig. 9B,  $\text{PbI}_2$  suffers photodecomposition to iodine gas ( $\text{I}_2$ ) and lead ( $\text{Pb}^0$ ) upon interaction with visible light.<sup>[135]</sup>  $\text{I}_2$  gas is released from  $\text{MAPbI}_3$  even in dark conditions during heating at temperatures as low as 40 °C to 80 °C, which correspond to solar cell working temperatures. Such intrinsic photolysis of  $\text{PbI}_2$  is related to the devices' instability under continuous light illumination.<sup>[135]</sup> Tumen-Ulzii et al.<sup>[141]</sup> further confirmed the detrimental effect of unreacted  $\text{PbI}_2$  on the long-term stability of PSCs. The PVK films were deposited from 1.12 M  $\text{Cs}_{0.05}(\text{FA}_{1-x}\text{MA}_x)_{0.95}\text{Pb}(\text{I}_{1-y}\text{Br}_y)_3$  precursor solution. Unreacted  $\text{PbI}_2$  were deposited at the surfaces and grain boundaries of PVK when the  $\text{PbI}_2$  concentrations in precursor solutions increased. The PCE of PSCs prepared with unreacted  $\text{PbI}_2$  reduced to 47%

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of its initial value after 520 h of continuous illumination. However, the PCEs of PSCs without unreacted  $\text{PbI}_2$  retained 99% of their initial values. SEM images revealed that unreacted  $\text{PbI}_2$  in the original PVK film almost disappeared, but defects and pinholes increased after 520 h of continuous illumination. They proposed that the degradation of  $\text{Cs}_{0.05}(\text{FA}_{1-x}\text{MA}_x)_{0.95}\text{Pb}(\text{I}_{1-y}\text{Br}_y)_3$  PSCs was due to the photolysis of unreacted  $\text{PbI}_2$  into  $\text{Pb}^0$  and  $\text{I}_2$  gas under light illumination.

In addition to  $\text{PbI}_2$ , alkali metal iodides are considered as important additives to enhance the performance of PVK, especially for eliminating hysteresis in PSCs. In 2017, Tang et al.<sup>[142]</sup> were the first to report hysteresis-free PVK solar cells after adding a small amount of KI (5%) into the  $(\text{FA}_{0.85}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3)$  PVK. With incorporation of KI, the electron transfer barrier between  $\text{TiO}_2/\text{PVK}$  is minimized, resulting in the elimination of  $J$ - $V$  hysteresis and a PCE of more than 20%. Then after, Abdi-Jalebi et al.<sup>[136]</sup> demonstrated that the KI fills the halide vacancies and acts as a passivation layer decorating the PVK surface and grain boundaries. As shown in Fig. 9C, the potassium-rich, halide-sequestering species at the grain boundaries and surfaces would inhibit halide migration and suppress any additional non-radiative decay arising from interstitial halides. They obtained a champion PCE of 21.5% with KI at ~9.09%, based on the  $(\text{Cs,FA,MA})\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$  PVK, with the elimination of PSC hysteresis. A series of alkali metal iodides of LiI, NaI, KI, RbI and CsI were introduced into PVK films by Cao et al.<sup>[143]</sup>. They demonstrated that alkali cations can occupy the interstitial sites of the PVK lattice and suppress ion migration, which results in elimination of  $J$ - $V$  hysteresis and enhancement of photostability of PSCs. On the other hand, Son et al.<sup>[137]</sup> found from DFT calculation that the hysteresis of PVK solar cells arises from the formation of iodide Frenkel defect not the migration of iodide vacancy. They compared the effect of adding alkali metal iodides (LiI, NaI, KI, RbI and CsI) in PVK material on reducing current–voltage hysteresis. KI was found the best candidate for preventing the formation of iodide Frenkel defect, because K interstitials are energetically the most stables. As a result, they prepared mixed PVK  $(\text{FA}_{0.875}\text{MA}_{0.125}\text{PbI}_{2.55}\text{Br}_{0.45})$  based PSCs with complete removal of hysteresis (Fig. 9D). Meanwhile, the alkali halide additive is able to homogenize the halide distribution, which help for the formation of uniform and continuous PVK film, leading to hysteresis-free PSCs with improved performance.<sup>[144, 145]</sup>

### 3.5 Pseudo-halides additives for PVK films

Pseudo-halides, such as thiocyanate ( $\text{SCN}^-$ ) or cyanide ( $\text{CN}^-$ ) have similar chemical behaviors and properties to halogen. The ionic radii of thiocyanate ( $\text{SCN}^-$ ) is ~217 pm, which is close to the iodine ionic radius of 220

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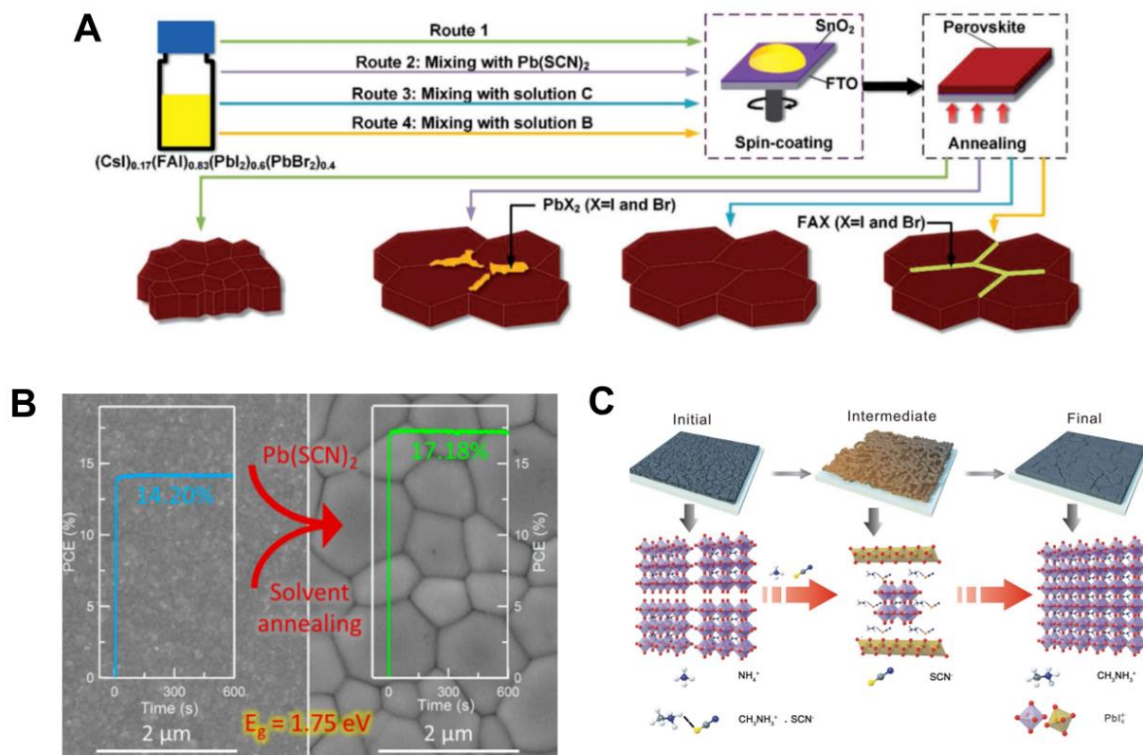
pm and is expected to act as a substitute of halogen atoms in halide PVK.<sup>[146-148]</sup> To date, various pseudo-halide, such as Pb(SCN)<sub>2</sub>, NH<sub>4</sub>SCN and MASCN, have been incorporated into PVK film to adjust the PVK crystal nucleation and growth process and passivate the crystal defects, effectively enhancing the performance of PSCs.

The incorporation of pseudo-halide in the PVK layer can improve the grain size, material crystallinity and optical properties of PVK layers.<sup>[149]</sup> In 2015, Halder et al.<sup>[146]</sup> reported that the incorporation of pseudo-halide in MAPbI<sub>3</sub> can increase the optical bandgap up to ~80 meV, and gives rise to a remarkable improvement in the photoluminescence (PL) emission quantum yield. Chen et al.<sup>[150]</sup> reported the two-step preparation of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>(SCN)<sub>x</sub> PVK via adding a small amount of Pb(SCN)<sub>2</sub> into PbI<sub>2</sub> solution. They revealed that the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>(SCN)<sub>x</sub> with optimized 5 wt% Pb(SCN)<sub>2</sub> leads notably to stronger absorption at 400-625 nm. In addition, Zhou et al.<sup>[151]</sup> compared several preparation routes for investigating the effect of Pb(SCN)<sub>2</sub> on the performance of PVK film (Fig. 10A). The Cs<sub>0.17</sub>FA<sub>0.83</sub>PbI<sub>3-x</sub>Br<sub>x</sub> (x=0.8) films deposited by the direct spin-coating of Cs<sub>0.17</sub>FA<sub>0.83</sub>PbI<sub>3-x</sub>Br<sub>x</sub> from (CsI)<sub>0.17</sub>(FAI)<sub>0.83</sub>(PbI<sub>2</sub>)<sub>1-0.5x</sub>(PbBr<sub>2</sub>)<sub>0.5x</sub> (precursor solution A) exhibited small grains and low crystallinity (Route 1). Then, they added 5 vol.% of Pb(SCN)<sub>2</sub> solution into solution A (Route 2). It led to increased grain size and crystallinity but PbX<sub>2</sub> (X = I and Br) impurity byproduct segregated randomly at the grain boundaries. Accordingly, they deposited PVK from (CsI)<sub>0.17</sub>(FAI)<sub>0.83</sub>(Pb(SCN)<sub>2</sub> + 2FAI)<sub>0.6</sub>(Pb(SCN)<sub>2</sub> + 2FABr)<sub>0.4</sub> (precursor solution C), in which the molar ratio FAX: Pb(SCN)<sub>2</sub> = 2:1. It resulted in a film with large grain size and high crystallinity without PbX<sub>2</sub>. Since the excess of MAX can passivate the defects, solution B but with higher FAX: Pb(SCN)<sub>2</sub> ratio to 3:1 (route 4) was used to deposit PVK film. Highly crystallized and large grain ~1300 nm PVK (Fig. 10A) was obtained by this Route 4. With the synergistic effects of Pb(SCN)<sub>2</sub> assisted crystallization and FAX grain boundary healing, the well-passivated PSC showed greatly reduced hysteresis and excellent photovoltaic performance.

Pb(SCN)<sub>2</sub> affects the reaction between PbI<sub>2</sub> and MAI, leading to the PbI<sub>2</sub> residual in the PVK films. PbI<sub>2</sub> is an undesirable byproduct that can be detected in the PVK film and which is detrimental for the stability of PSC. Yu et al.<sup>[152]</sup> developed an efficient strategy combining Pb(SCN)<sub>2</sub> additive (1.0 mol % Pb(SCN)<sub>2</sub>) and a solvent annealing process to get large PVK grain size and avoiding PbI<sub>2</sub> excess formation (Fig. 10B). As a result, the average grain size of wide-bandgap FA<sub>0.8</sub>Cs<sub>0.2</sub>Pb(I<sub>0.7</sub>Br<sub>0.3</sub>)<sub>3</sub> PVK thin films ( $E_g = 1.75$  eV) increased from  $66 \pm 24$  to  $1036 \pm 317$  nm, and the mean carrier lifetime increased by more than 3-fold, from 330 to over 1000 ns. Kim et al.<sup>[153]</sup> developed (FA<sub>0.65</sub>MA<sub>0.20</sub>Cs<sub>0.15</sub>)Pb(I<sub>0.8</sub>Br<sub>0.2</sub>)<sub>3</sub> PSCs with an PCE of ~20% by using PEAI and Pb(SCN)<sub>2</sub> as additives. The cooperation of PEA<sup>+</sup> and SCN<sup>-</sup> provided a synergistic effect that enhanced

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PVK morphology and reduced  $\text{PbI}_2$  formation. As a result, using both additives increased the charge-carrier mobility and lifetime of PVK to near  $50 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and  $3 \mu\text{s}$ , higher values than that of control samples. The average PCE of PSCs increased from 16.3% to 18.7%.



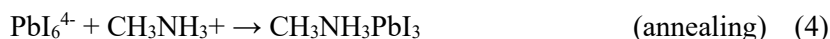
**Fig. 10** (A) Schematics of different routes to prepare the  $\text{FA}_{0.17}\text{Cs}_{0.83}\text{PbI}_{3-x}\text{Br}_x$  ( $x = 0.8$ ) PVK thin films.<sup>[151]</sup> with permission from Wiley-VCH, copyright 2018. (B) SEM images of  $\text{FA}_{0.8}\text{Cs}_{0.2}\text{Pb}(\text{I}_{0.7}\text{Br}_{0.3})_3$  PVK thin films before and after the synergistic effects of  $\text{Pb}(\text{SCN})_2$  and solvent annealing process.<sup>[152]</sup> with permission from the American Chemical Society, copyright 2017. (C) Schematic diagram of the recrystallization process: morphological evaluation and structure dynamic process of the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  film with  $\text{NH}_4\text{SCN}$  treatment.<sup>[154]</sup> with permission from Wiley-VCH, copyright 2017.

In addition to  $\text{Pb}(\text{SCN})_2$ , volatile additives such as  $\text{NH}_4\text{SCN}$  and  $\text{MASCN}$  have also been adopted to improve the crystallinity of PVK films and enhance cells performance.<sup>[154, 155]</sup> Dong et al.<sup>[154]</sup> demonstrated a  $\text{NH}_4\text{SCN}$ -induced recrystallization process (Fig. 10C) through an antisolvent method for improving the morphology and crystalline quality of the PVK film. First, when the prepared  $\text{MAPbI}_3$  (Initial film) was dipped into  $\text{NH}_4\text{SCN}$  in IPA solution, it was partially dissolved and formed the mesoporous framework (Intermediate film) with  $\text{PbI}_2$  compound. Since  $\text{SCN}^-$  has a stronger ionic bonding with  $\text{CH}_3\text{NH}_3^+$  than  $\text{I}^-$ ,  $\text{CH}_3\text{NH}_3^+$  is preferred to form ionic bonding with  $\text{SCN}^-$  than  $\text{I}^-$  in this intermediate state (Equation 2). Upon the annealing process, the formed  $\text{NH}_3$  and  $\text{HSCN}$  volatilized quickly (Equation 3). Subsequently, the undissolved polycrystal could play the role of



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nucleus for the recrystallization process, new well-crystallized MAPbI<sub>3</sub> (Final film) was formed and PbI<sub>2</sub> impurity disappeared (Equation 4).



As a result, MAPbI<sub>3</sub> prepared through such intermediate catalytic effect of NH<sub>4</sub>SCN exhibited large crystal grain sizes, as well as lower trap density, leading to a higher PCE of 19.44%. NH<sub>4</sub>SCN additive strategy was also used in Cs-based and Sn-based PVK films for improving the crystallinity, stability and oxidation resistance in air atmosphere, promoting charge transfer and performances of devices.<sup>[156, 157]</sup>

Zhang et al.<sup>[158]</sup> employed ammonium thiocyanate (NH<sub>4</sub>SCN) as additive for the preparation of MAPbX<sub>3</sub> layers. This compound was the most efficient at 15 mol% in the PPS and provided better benefits compared to NH<sub>4</sub>I or Pb(SCN)<sub>2</sub> additives. They showed a synergistic effect of both cation and anion for the control of the nucleation and growth of the perovskite layer which gave rise to bigger grains and more stable layers. The final composition of the layer was MAPbI<sub>3-x</sub>SCN<sub>x</sub> and these authors showed the formation of the NH<sub>4</sub>PbI<sub>3-x</sub>SCN<sub>x</sub> intermediate, more stable than the MAPbI<sub>3</sub> one. It induces less defects and slow down the rate of crystallization. They have also linked the good stability of MAPbI<sub>3-x</sub>SCN<sub>x</sub> with the linear shape of SCN<sup>-</sup> ions, strongly coordinated with Pb<sup>2+</sup> ions.

The list of the main other halides and pseudo-halides employed as additives for PSC, the cell structure, PCEs and *J-V* curve parameters are gathered in the Table 4.

We have reported that fluoride species can form strong ionic and intermolecular bonding with PVK, which is beneficial for passivating surface and crystal boundaries defects. They can endow the surfaces with hydrophobic properties and then protect the PVK from moisture erosion. In lead-free PVK, SnF<sub>2</sub> can suppress the oxidation from Sn<sup>2+</sup> to Sn<sup>4+</sup>, reducing the background carrier density and Sn defects for improving the performance of Sn-based PSCs. Bromide additives can broaden the band gap of PVK, control the PVK growth to get large grains. They passivate grain boundaries, passivate defects related to Sn<sup>2+</sup> oxidation. It results in longer lifetimes, improve stability. Iodide additives act as candidates for preventing the formation of iodide Frenkel defect, forming uniform and continuous PVK film and leading to hysteresis-free PSCs with improved performances. Regarding pseudo-halides, they can act as a substitute of halogen atoms in the halide PVK, and the incorporation of pseudo-halide can improve the grain size, material crystallinity and optical properties of PVK layers.

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**Table 4.** Other halides and pseudo-halides additives used in PVK, concentration, cell structure, PCE and J-V curve parameters.

Other halides and pseudo-halides additives in the bulk	Concentration	Device structure	PCE (%)	J <sub>sc</sub> (mA.cm <sup>-2</sup> )	V <sub>oc</sub> (V)	FF (%)	Year <sup>Ref.</sup>
SnF <sub>2</sub>	20 mol%	FTO/TiO <sub>2</sub> /MASnI <sub>3</sub> /PTAA/Au	1.94	26.1	0.25	30.00	2017 <sup>[100]</sup>
SnF <sub>2</sub> -Pyrazine	20 mol%	FTO/TiO <sub>2</sub> /FASnI <sub>3</sub> /Spiro-OMeTAD/Au	4.00	24.5	0.29	55.00	2016 <sup>[103]</sup>
NaF	0.1 mol%	ITO/SnO <sub>2</sub> /(Cs <sub>0.05</sub> FA <sub>0.54</sub> MA <sub>0.41</sub> )Pb(I <sub>0.98</sub> Br <sub>0.02</sub> ) <sub>3</sub> /spiro-OMeTAD/	21.92	24.23	1.126	80.35	2019 <sup>[105]</sup>
NbF <sub>5</sub>	3 mg.mL <sup>-1</sup>	FTO/TiO <sub>2</sub> /PVK(NbF <sub>5</sub> )/PCBM/Ag	20.56	25.4	1.05	77.08	2019 <sup>[106]</sup>
guanidinium bromide (GABr)	12 mol%	ITO/EMIC-PEDOT:PSS/FA <sub>0.7</sub> MA <sub>0.3</sub> Pb <sub>0.7</sub> Sn <sub>0.3</sub> I <sub>3</sub> /S-acetylthiocholine chloride passivation layer /C60/BCP/Ag	20.63	26.61	1.02	76.00	2020 <sup>[119]</sup>
N-(4-bromophenyl)-thiourea (BrPh-ThR)	0.6 mg.mL <sup>-1</sup>	FTO/TiO <sub>2</sub> /(FAI) <sub>0.81</sub> (PbI <sub>2</sub> ) <sub>0.85</sub> (MABr) <sub>0.15</sub> (PbBr <sub>2</sub> ) <sub>0.15</sub> /Spiro-OMeTAD/Au	21.7	23.93	1.12	78.00	2018 <sup>[120]</sup>
RbI; CsI	5 mol%; 5 mol%	FTO/TiO <sub>2</sub> /(MAPbBr <sub>3</sub> ) <sub>0.17</sub> (FAPbI <sub>3</sub> ) <sub>0.83</sub> /Spiro-OMeTAD/Au	19	22.7	1.1	76.00	2019 <sup>[145]</sup>
ethylenediammonium diiodide	1 mol%	ITO/PEDOT:PSS/FASnI <sub>3</sub> /C60 /BCP/Ag	8.9	21.3	0.583	71.80	2018 <sup>[159]</sup>
MASCN	40 mol%	FTO/TiO <sub>2</sub> /MAPbI <sub>3</sub> /Spiro-OMeTAD/Au	18.22	23.2	1.064	76.94	2017 <sup>[155]</sup>
PEAI; Pb(SCN) <sub>2</sub>	1 mol%; 2 mol%	ITO/PTAA/(FA <sub>0.65</sub> MA <sub>0.20</sub> Cs <sub>0.15</sub> )Pb(I <sub>0.8</sub> Br <sub>0.2</sub> ) <sub>3</sub> /C60/BCP/Ag	19.8	21.2	1.17	79.80	2019 <sup>[153]</sup>
FASCN; PEA	5 mol%; 10 mol%	ITO/PEDOT:PSS/FASnI <sub>3</sub> /PCBM/Al	8.17	22.5	0.53	68.30	2018 <sup>[160]</sup>
Pb(SCN) <sub>2</sub>	2 mol%	FTO/PEALD SnO <sub>2</sub> /C60-SAM/(MA <sub>0.7</sub> FA <sub>0.3</sub> PbI <sub>3</sub> ) <sub>1-x</sub> (CsPbI <sub>3</sub> ) <sub>x</sub> /spiro-OMeTAD/Au	20.49	23.05	1.11	80.09	2018 <sup>[161]</sup>
GuaSCN	7 mol%	ITO/PEDOT:PSS/(FASnI <sub>3</sub> ) <sub>0.6</sub> (MAPbI <sub>3</sub> ) <sub>0.4</sub> /C60/bathocuproine/Ag	18.7	28.7	0.82	79.00	2019 <sup>[118]</sup>
NH <sub>4</sub> SCN	1.5 mol%	ITO/TiO <sub>2</sub> /CsPbBr <sub>3</sub> /Spiro-OMeTAD/Au	8.47	7.76	1.375	79.31	2020 <sup>[156]</sup>
NH <sub>4</sub> SCN	0.03 M.mL <sup>-1</sup>	ITO/PTAA/CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> /PCBM/BCP/Ag	19.44	22.55	1.103	78.20	2017 <sup>[154]</sup>
NH <sub>4</sub> SCN	15 mol%	ITO/PEDOT:PSS/ MAPbI <sub>3-x</sub> SCN <sub>x</sub> /PC61BM/LiF/Al	16.47	23.31	0.96	73.84	2018 <sup>[158]</sup>
Pb(SCN) <sub>2</sub>	2 mol%	FTO/TiO <sub>2</sub> /CsPbI <sub>3</sub> /PTAA/Au	17.03	20.34	1.09	77.00	2019 <sup>[162]</sup>



## 4. Halides at the interfaces of PSCs

The ETL/PVK and HTL/PVK interfaces play a critical role on the performances of PSCs. They must be engineered to improve the PSC characteristics. Especially, interfacial modification is key to passivate the defects of metallic oxide ETL and PVK, improving the charge transfer and reducing the charge recombination. Moreover, they can induce PVK crystal modification, adjustment of the energy-level alignment and the stabilization of the PVK towards UV-light, humidity and oxygen degrading agents. Normally, the modification is obtained by adding the halide additive into the charge carrier precursor solution, spin-coating halide additive solution onto the charge carrier layers or by soaking the well-formed layer in an additive solution.

### 4.1 Introduction of halogen atoms at the ETL/PVK interface

Chlorine serves as contact passivator to mitigate the interfacial recombination. Defects at the ETL/PVK interface and induces charge recombination which has a negative effect on the performance and stability of PSCs and that must be addressed by passivating the surface of active layers. Tan et al.<sup>[163]</sup> employed chlorine-capped TiO<sub>2</sub> colloidal nanocrystal to suppress TiO<sub>2</sub> deep trap states and reduce the interface recombination at the TiO<sub>2</sub>/PVK contact. DFT calculation showed that Cl at the interface results in a lower density of interfacial trap states, as well as in a stronger binding of PVK to TiO<sub>2</sub> interface. As a result, the hysteresis-free planar PSCs with champion PCE of 20.1% for small-area devices (0.049 cm<sup>2</sup>) was obtained. F doping of SnO<sub>2</sub> was used to adjust the Fermi level of ETL.<sup>[164]</sup> The device  $V_{oc}$  could be tailored by modulating the band offset at the interface of ETL and PVK. The grain boundary barriers and defects within the bilayer ETL could be largely restrained due to a matched lattice constant.

### 4.2 Halides at the ETL/PVK interface

Organic monolayer on ETL surface have been introduced to enhance the interfacial optoelectronic properties of PSCs. The metallic oxide and PVK can undergo chemical interaction with organic molecules, which can improve the PVK film quality and promote the electron extraction while

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restricting the charge recombination between ETL and PVK. With this motivation, organic small molecular materials have been used for interfacial modification such as benzoic acid derivatives onto the TiO<sub>2</sub> in PSCs.<sup>[165]</sup> Pauporté et al.<sup>[166]</sup> investigated the effect of self-assembled monolayers (SAMs) prepared by spin-coating benzoic acid derivatives onto the TiO<sub>2</sub> of PSCs. As shown in Fig. 11A, a series of organic compounds with benzene and various terminal groups were tested (Cl, NO, Br, O-CH<sub>3</sub>, NH<sub>2</sub>) and compared to β-alanine, an amino acid. The –COO anchoring group passivates the ETL surface via chemical bonding. The best functional group was found to be Cl (CBA) with a stabilized PCE reaching 20.9% (20.0% for the pristine cell). The para-Cl group can establish a stable bonding with the PVK. The presence of this monolayer decreased interfacial trap states, improved the global PVK quality and created a structural continuity between TiO<sub>2</sub> and PVK. This system was further studied by DFT<sup>[167]</sup> that showed the bonding between Cl and Pb of the PVK (Fig. 11B). The computed density of states revealed that the PVK (MAPbI<sub>3</sub> employed as a model PVK) contributes to the top of the valence band while TiO<sub>2</sub> ETM contributes to the bottom of the conduction band. It indicated that an electron transfer from MAPbI<sub>3</sub> to TiO<sub>2</sub> is possible. Furthermore, these authors quantified the spin density of the reduced MAPbI<sub>3</sub>/CBA/TiO<sub>2</sub> system and calculated a quantitative (99.94%) electron transfer from MAPbI<sub>3</sub> to TiO<sub>2</sub> to the interfacial engineering. They have also calculated an ultrafast electron injection time at 24 fs, and the dipole moment of 0.61 D induced by CBA at the interface which is favorable for the charge transfer from MAPbI<sub>3</sub> to TiO<sub>2</sub>.

Introducing inorganic metal halide materials at the ETL/PVK interface can adjust the band alignment, passivate the surface trap states and suppress the recombination process. As shown in Fig. 11C, p-type CuI on TiO<sub>2</sub> surface was used to modify the TiO<sub>2</sub> band alignment by shifting the conduction band bottom from -4.13eV to -3.93eV. It resulted in a barrier-free contact and an increased open-circuit voltage. Meanwhile, the polarity of the CuI-modified TiO<sub>2</sub> surface was favorable to pull electrons from PVK to the interface of ETL/PVK, improving electron extraction and reducing nonradiative recombination.<sup>[168]</sup> In a similar manner, inorganic alkaline halide was used to passivate ionic defects with their cations and anions. Li et al.<sup>[169]</sup> introduced CsBr onto the compact c-TiO<sub>2</sub> surface in planar heterojunction solar cells, which reduced the pinholes density and resulted in the shifts of work function of TiO<sub>2</sub> from 4.07 to 3.09 eV. Such CsBr surface modification enhanced the electron transfer and the stability of planar heterojunction devices under ultraviolet (UV) light soaking. It is reported that alkaline halides can

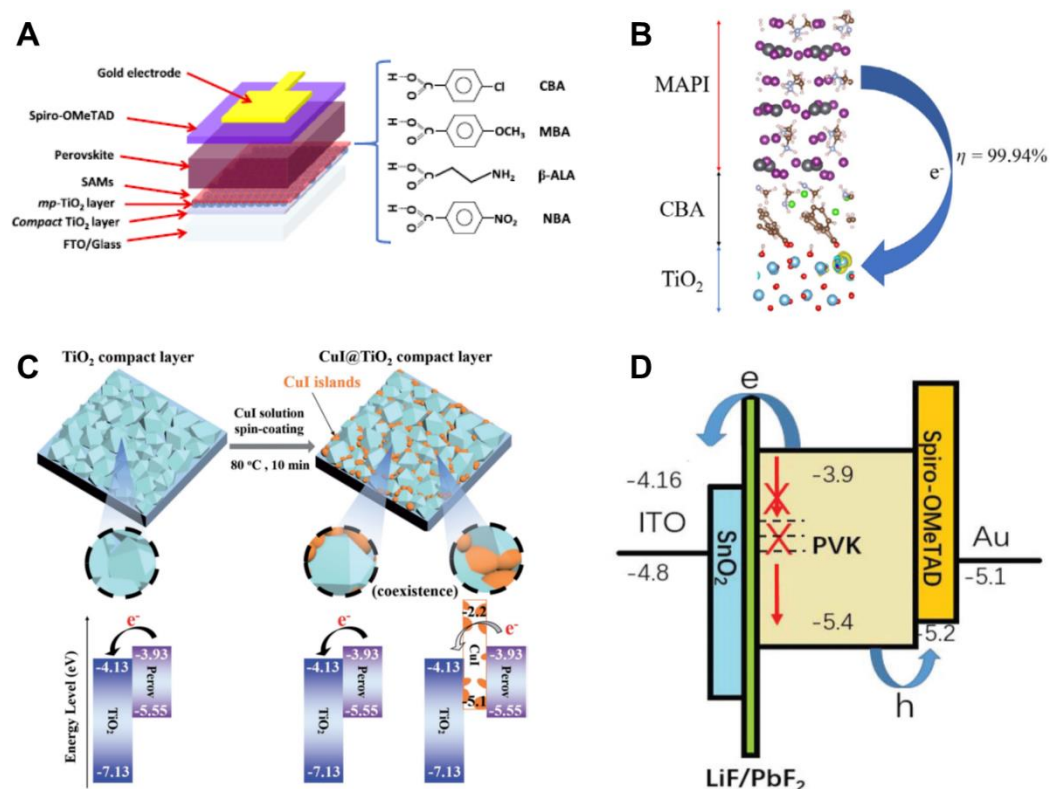
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passivate both types of charged defects (positive and negative) with alkaline cation and halide anion. Yuan et al.<sup>[170]</sup> demonstrated the interfacial passivation effect of LiF at the SnO<sub>2</sub>/PVK interface (Fig. 11D). The intermediate layer of LiF effectively blocks holes and promotes the electron transport. In order to identify the interfacial passivation by Li<sup>+</sup> and F<sup>-</sup>, devices with PbF<sub>2</sub> (F<sup>-</sup> only) or LiTFSI (Li<sup>+</sup> only) modified layer were fabricated. It was found that F<sup>-</sup> ion play a main role in the device performance improvement. Hysteresis-less planar PSCs with a PCE of 18.3% were fabricated by Ma et al.<sup>[171]</sup> via passivating the compact TiO<sub>2</sub>/PVK interface with NaCl. They immersed the TiO<sub>2</sub> substrate in 0.5 mg.mL<sup>-1</sup> NaCl solution and then heated at 500 °C for 15 min. By varying light intensities from 0.1 to 100 mW cm<sup>-2</sup>, the  $V_{oc}$  versus light intensity slope of the devices based on pristine TiO<sub>2</sub> and NaCl modified TiO<sub>2</sub> were 1.23 kT/q and 1.14 kT/q, respectively (where k is the Boltzmann constant, T is absolute temperature, and q is the elementary charge). It indicated that the doping treatment reduced the trap density at the TiO<sub>2</sub>/PVK interface and improved the electrical property of TiO<sub>2</sub>. To further understand the mechanism of charge transfer and recombination, transient photocurrent (TPC) under short-circuit condition and transient photovoltage (TPV) under open-circuit conditions measurements were performed. TPC decay lifetime was faster at 0.51 μs for TiO<sub>2</sub>-NaCl while TPV exhibited a longer decay lifetime of 24.67 μs for TiO<sub>2</sub>-NaCl. It indicated more efficient charge transfer, extraction process and efficient suppression of charge recombination, respectively. The hysteresis index was reduced from 12.6% to 2.7% after the doping treatment. The trap density of TiO<sub>2</sub> and TiO<sub>2</sub>-NaCl measured by space charge limited current (SCLC) were 7.08×10<sup>16</sup> cm<sup>-3</sup> and 5.19×10<sup>16</sup> cm<sup>-3</sup>, respectively. The electron mobility of TiO<sub>2</sub>-NaCl increased to 7.20×10<sup>-4</sup> cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> compared to that of pristine TiO<sub>2</sub> (3.48×10<sup>-4</sup> cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>). Finally, the film was more homogeneous after NaCl doping.

Jang et al.<sup>[172]</sup> developed a deposition and diffusion method of alkaline chlorides onto ZnO ETL to effectively passivate both shallow and deep trap states, which were present in PVK crystallized layer and at the PVK/ETL interface. Dual trap passivation dramatically improved the PCE, reduced the photocurrent hysteresis, and enhanced the long-term stability of PSCs. The ZnO layers were modified by immersing them in aqueous alkaline chloride (LiCl, NaCl, KCl, CsCl), the reduction in defect-related PL emissions was the most prominent in the 10 mM KCl modified ZnO sample. Interfacial defect passivation was due to both K and Cl. As a result of time-correlated single-photon counting (TCSPC) analysis, the ZnO-KCl sample exhibited a substantially shorter decay time (2.73 ns). The charge

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recombination lifetime and charge transport time of the modified PSCs were 204  $\mu$ s and 1.7  $\mu$ s, respectively. The average grain size of the KCl modified PVK sample was about 450 nm, whereas that of the unmodified sample was about 300 nm. TEM coupled with EDS mapping showed the penetration of K and Cl atoms throughout the PVK layers. The KCl modified low-temperature processed PSCs (L-PSC) achieved the highest PCE of 22.6%. With an active area of 1.12 cm<sup>2</sup>, L-PSC-KCl reached 21.3%, which was one of the highest values among the reported L-PSCs with an active area of >1 cm<sup>2</sup> thus far. The long-term shelf-life of unencapsulated L-PSCs was tested following the ISOSD-1 protocol (in the dark, 25 °C, 40% humidity, in air).<sup>[173]</sup> The L-PSC-KCl maintained 90% of its initial PCE after 1400 h. Moreover, Liu et al.<sup>[174]</sup> also observed that the inorganic binary alkaline halide salts treatment of the SnO<sub>2</sub>/PVK interface can significantly increase the open-circuit voltage and eliminate hysteresis.



**Fig. 11** (A) PSC cell structure and mesoporous *mp*-TiO<sub>2</sub> layer covered by SAMs (in red) of *para*-substituted benzoic acid derivatives and  $\beta$ -alanine.<sup>[166]</sup> with permission from The American Chemical Society, copyright 2020. Spin density of the reduced MAPI-CBA-TiO<sub>2</sub> interface system and calculated charge injection efficiency.<sup>[167]</sup> with permission from Wiley-VCH, copyright 2020. (C) Schematic illustration of the deposition of CuI on TiO<sub>2</sub> compact layer. In CuI@TiO<sub>2</sub>-based devices, electrons transfer from PVK to exposed TiO<sub>2</sub> not CuI due to the high conduction band energy level of CuI.<sup>[168]</sup> with permission from Wiley-VCH, copyright 2018 (D) Structure of the PSC with a thin layer of LiF or PbF<sub>2</sub> on SnO<sub>2</sub> layer.<sup>[170]</sup> with permission from The Royal Society of Chemistry, copyright 2018.

### 4.3 PVK layer surface engineering

Due to the ionic nature of PVK materials, undesirable electronic defects and pinholes can be observed at the surface and grain boundaries of PVK layers. Such defects decrease the charge collection efficiency and increase the charge recombination during the photoelectric conversion process, the best performance of PSCs still lags behind the theoretical limit of Shockley–Queisser efficiency. Moreover, the crystal defects and uncoordinated ions at the surface and grain boundaries are supposed to affect the stability of PSCs. Thus, in order to develop the high-efficiency and stable PSCs, it is essential to passivate the crystal defects at the crystal surface and grain boundaries.

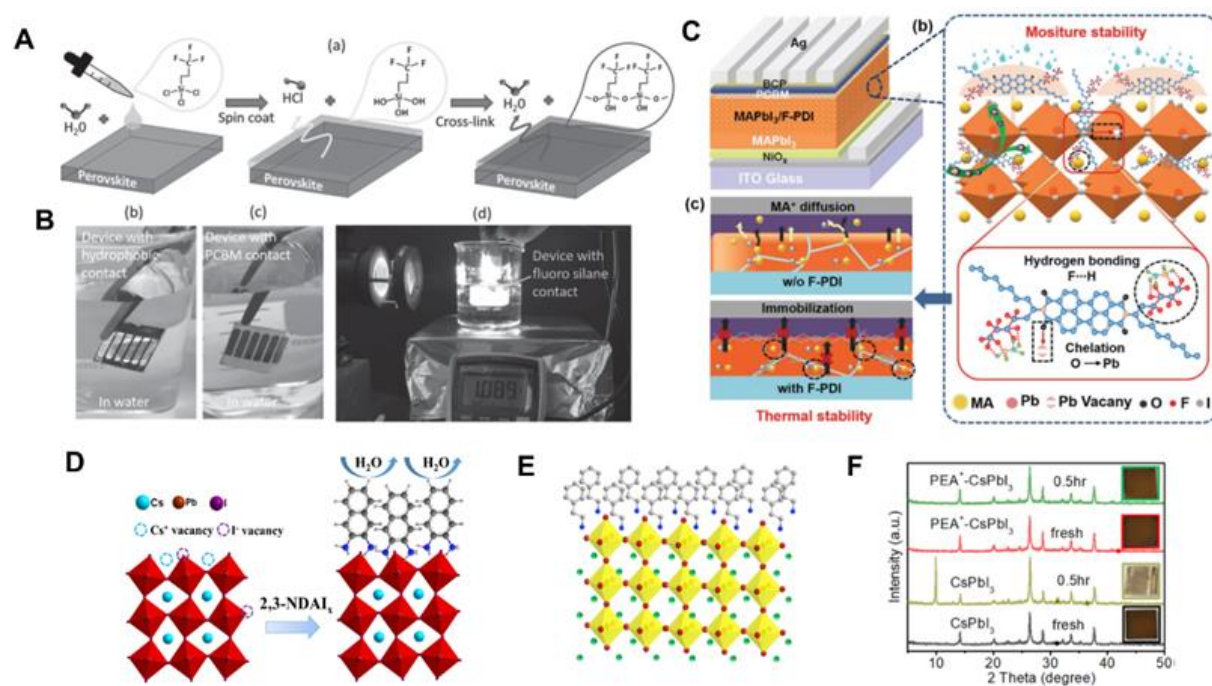
#### 4.3.1 Hydrophobic organo-halogen at the surface of PVK

Some organic insulating tunneling layers consisting of hydrophobic groups can cover the surface of PVK film, suppressing carrier recombination and protecting the PVK from decomposition caused by moisture. The fluorinated organic compounds are known to be hydrophobic, and have been used to improve the stability of PVK by grafting on the surface of PVK crystals. Wang et al.<sup>[175]</sup> chose a hydrophobic insulating fluoro-silane, trichloro(3,3,3-trifluoropropyl)silane, as a tunneling layer deposited on the top of MAPbI<sub>3</sub> PVK film to fabricate water-resistant devices (Fig. 12A). As shown in Fig. 12B, the silanes were hydroxylated to the silanols with tiny amount of H<sub>2</sub>O. Then, they underwent a cross-linking by forming Si-O-Si bonds, this fluoro-silane insulating organic layer protected the underneath PVK films from water attack. Meanwhile, this tunneling layer spatially separated photogenerated electrons and holes at the PVK/polymer HTM interface. It reduced the carrier surface recombination and significantly increased the device performance. Considering the conductivity of fluorinated compounds, the conductive fluorinated perylenediimide (F-PDI) was introduced to fill in at grain boundaries and surface of the PVK film (Fig. 12C).<sup>[176]</sup> The conductive F-PDI chemical bonding to PVK film effectively passivated defects and promoted the charge transport. Meanwhile, hydrogen bond formed between F-PDI and MA<sup>+</sup> reduced the mobility of MA<sup>+</sup> in the MAPbI<sub>3</sub> PVK and therefore improved the thermal and moisture stability. F-PDI-incorporated device based on the



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(FA<sub>0.83</sub>MA<sub>0.17</sub>)<sub>0.95</sub>Pb(Br<sub>0.17</sub>I<sub>0.83</sub>)<sub>3</sub> absorber showed champion efficiencies of 19.26%, and maintains 80% of its initial efficiency even after exposure to RH of 50% for 30 days. In another work, Wu et al.<sup>[177]</sup> developed a CF<sub>4</sub> plasma treatment for fluorinating the whole PSC device. A strongly bonded C-F<sub>x</sub> layer covered the top and lateral surface of PSCs, which exhibited an excellent water-repellent property, without any change after immersion into water for 5 min. Liu et al.<sup>[178]</sup> introduced a two-dimensional (2D) A<sub>2</sub>PbI<sub>4</sub> PVK layer using pentafluorophenylethylammonium (FEA) as a fluoroarene cation inserted between the 3D light-harvesting PVK film and the hole-transporting material (HTM). The perfluorinated benzene moiety conferred an ultra-hydrophobic character to the spacer layer, protecting the PVK material from ambient moisture while mitigating ionic diffusion in the device.



**Fig. 12** (A) Schematic illustration for the cross-link process of fluoro-silane layer on the PVK film. (B) The humidity stability test for the PVK layers with and without fluoro-silane contact.<sup>[175]</sup> with permission from Wiley-VCH, copyright 2016. (C) Schematic illustration of PSCs structure, the interactions between F-PDI and MAPbI<sub>3</sub> PVK.<sup>[176]</sup> with permission from Wiley-VCH, copyright 2019. (D) Schematic illustration of defect passivation and water resistance effect with naphthalenediammonium iodide.<sup>[191]</sup> with permission from The Royal Society of Chemistry, copyright 1996. (E) Schematic illustration of PEA<sup>+</sup> cations at CsPbI<sub>3</sub> surface termination (F) XRD patterns and photographs of the CsPbI<sub>3</sub> and PEA<sup>+</sup>-CsPbI<sub>3</sub> thin films after exposed to ambient environment with 85%–90% RH at RT for 0.5 hr.<sup>[179]</sup> with permission from Elsevier, copyright 2018.



### 4.3.2 Passivation of PVK defects and near surface film modification

It is known that the imperfections in hybrid perovskite could induce a large density of traps. There are three types of defects in the  $\text{MAPbI}_3$ : vacancies ( $V_{\text{MA}}$ ,  $V_{\text{Pb}}$ ,  $V_{\text{I}}$ ), interstitials ( $\text{MA}_i$ ,  $\text{Pb}_i$ ,  $\text{I}_i$ ) and antisite substitutions ( $\text{MA}_{\text{Pb}}$ ,  $\text{Pb}_{\text{MA}}$ ,  $\text{MA}_{\text{I}}$ ,  $\text{Pb}_{\text{I}}$ ,  $\text{I}_{\text{MA}}$ ,  $\text{I}_{\text{Pb}}$ ), where in the latter  $\text{A}_B$  indicates that A is substituted by B. The first-principles calculations are performed to investigate the electronic structure, dielectric properties and defect properties of perovskite. Buin et al.<sup>[180]</sup> showed the origin of major sources of deep traps for the perovskite materials *via* analysis of defect aggregation in terms of defect binding energies with DFT calculations. They concluded that the halide vacancies are the major source of deep traps in Cl-based perovskite, while lead interstitials are the dominant source of defects in Br-based perovskites. M. H. Du<sup>[181]</sup> calculated defects in  $\text{MAPbI}_3$  and showed that iodine vacancy is a low energy deep trap and non-radiative recombination centre. Thus, alloying iodide with chloride can reduce the lattice constant of the iodide and increases the formation energy of interstitial defects. As mentioned above, excess of halide or using mixed halides approach can prevent the formation of deep energy level.

Contrary to organo-halogen molecules, halide compounds are often used to passivate Pb interstitial and halide vacancies. Ammonium derivative halide salts are popular passivators that can reduce the cation and anion defects at PVK/HTL interface through hydrogen bonding or ionic bonding with PVK bulk. Until now, PTN-Br,<sup>[182]</sup> MAI,<sup>[183]</sup> FABr,<sup>[184]</sup> phenyltrimethylammonium bromide (PTABr),<sup>[185]</sup> imidazolium iodide (IAI),<sup>[186]</sup> ethylammonium iodide (EAI),<sup>[187]</sup> guanidinium hydroiodide (GAI),<sup>[188]</sup>  $\text{NH}_4\text{F}$ ,<sup>[189]</sup> Phenylhydrazinium iodide (PHAI),<sup>[190]</sup> Phenylethylammonium iodide (PEAI),<sup>[67]</sup> Naphthalenediammonium (2,3-NDA<sup>x+</sup>),<sup>[191]</sup> 5-Ammonium valeric acid iodide (5-AVAI),<sup>[192]</sup> n-propylammonium iodide (PAI) and propane-1,3-diammonium iodide (PDAI<sub>2</sub>)<sup>[67]</sup> have been notably inserted between PVK/HTL interface to passivate defects and to accelerate the carrier transfer to the contact and to reduce the recombination in devices. Among those, PTABr on  $\text{CsPbI}_3$  only induces a less than 5 nm blue shift in UV–vis absorbance, while the gradient of Br doping on the surface enhances the phase stability and significantly improves the stability of PSCs.<sup>[185]</sup> Wang et al.<sup>[193]</sup> reported that choline iodide (CHI) treatment of  $\text{CsPbI}_3$  increases the charge carrier and improves the energy-level alignment of PVK/ETL interface by 120 mV. PCE of CHI-modified PSCs reached 18.4%. Zhang et al.<sup>[191]</sup> introduced the  $\pi$ -conjugated naphthalenediammonium onto the surface of  $\text{CsPbI}_3$  PVK film *via*

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anchoring ammonium groups occupying A-site vacancies (**Fig. 12D**). This strategy largely improved humidity stability of CsPbI<sub>3</sub> PVK film and gave highly reproducible inorganic PSCs with a champion stabilized efficiency of 16.69% and a  $V_{oc}$  of 1.08V. Zheng et al.<sup>[194]</sup> reported that choline zwitterions, such as L-a-phosphatidylcholine, choline chloride and choline iodide, can effectively passivate ionic defects in hybrid PVK with their negative- and positive-charged components. This defect passivation reduced the open-circuit-voltage deficit of PSCs to 0.39V, boosted the PCE up to 20.66 % and enhanced the stability of films in ambient conditions. However, the mechanism of passivation effect with organic halide salts is not clear.

For the organic-inorganic hybrid PVK, a thin layer of 2D PVK can be formed on top of 3D PVK after post-treatment with an isopropyl alcohol (IPA) solution containing bulky organic cations ammonium. In this case, IPA partly dissolves the organic cation and favors the generation of a surface layer.<sup>[67]</sup> This layer improves the interface between the PVK and the HTL. PEAI has attracted much attention for the passivation of the PVK grain boundaries and surfaces in several studies.<sup>[67, 195]</sup> You et al.<sup>[37]</sup> found that PEAI itself can effectively passivate the PVK defects and therefore improves the efficiency of the devices. PEAI can also form a (PEA)<sub>2</sub>PbI<sub>4</sub> 2D PVK layer after reaction with I and Pb sources.<sup>[156]</sup> Pauporté et al.<sup>[67]</sup> employed PEAI to treat FA<sub>0.94</sub>MA<sub>0.06</sub>PbI<sub>3</sub> PVK layers. They showed that this treatment, without any thermal annealing, leads to the spontaneous formation of a crystallized (PEA)<sub>2</sub>PbI<sub>4</sub> 2D PVK nanolayer at the PVK film surface due to partial organic cation dissolution. It favored a fast transfer of photogenerated holes toward the HTL and reduced the recombination at and near the PVK/HTL interface in PSCs. The solar cell PCE was improved from 20.4% to 22.2% and the hysteresis became negligible. However, the reaction of PEAI seems to depend on the type of PVK. Actually, Wang et al.<sup>[179]</sup> demonstrated that CsPbI<sub>3</sub> could not cation exchange with PEAI to form 2D PVK layer, the PEAI on the CsPbI<sub>3</sub> layer just formed a surface termination layer (**Fig. 12E**), which enhanced phase stability and moisture resistance (**Fig. 12F**). Li et al.<sup>[197]</sup> investigated the surface treatment of methylammonium-free PVK layers by PAI and propane-1,3-diammonium (PDA) iodide. They observed a boosting of the PCE and an improvement of the solar cell stability for both treatments compared to the untreated PVK layer. Exceptional thermal and humidity stabilities were attained with PDA.

Hybrid 3D/2D PVKs possess longer carrier lifetimes and lower defect densities.<sup>[198, 199]</sup> Chen et al.<sup>[192]</sup> prepared a versatile ultrathin 2D PVK (5-AVA)<sub>2</sub>PbI<sub>4</sub> layer by spin-coating 5-AVAI solution on the

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(FAPbI<sub>3</sub>)<sub>0.88</sub>(CsPbBr<sub>3</sub>)<sub>0.12</sub>, which suppressed ion migration and improved interfacial charge extraction efficiency. Meanwhile, 5-AVA-modified devices showed enhanced moisture stability and photostability due to the excellent moisture stability of hydrophobic nature of interfacial 2D layer. So far, many ammonium halide salts such as n-hexyl trimethyl ammoniumbromide,<sup>[200]</sup> n-hexylammonium bromide,<sup>[201]</sup> cyclopropylammonium iodide,<sup>[202]</sup> alkyl ammonium bromides,<sup>[203]</sup> diethylenetriamine<sup>[204]</sup> have been employed to construct 2D PVK layer between PVK and HTL interface for improving performances of PSCs.

#### 4.4 HTL surface engineering

HTLs play a key role in extracting and transporting the holes in the photoconversion process of PSCs. Among a variety of HTMs, organic poly(bis(4-phenyl)-(2,4,6-trimethylphenyl)amine) (PTAA), 2,2',7,7'-tetrakis(N,N-di(4-methoxyphenyl)amino)-9,9'-spirobifluorene (Spiro-MeOTAD) and inorganic NiO<sub>x</sub>, CuSCN are the most common. In order to achieve high performance of PSCs, considerable efforts, *i.e.* additives, interface treatment, new materials have been successfully made to enhance energy alignment at HTL interface, thermal/photochemical stability, hole mobility and electrical conductivity of HTLs.

Modified HTLs materials with organo-halogen molecular doping is an efficient strategy to increase the performances of PSCs. Chen et al.<sup>[205]</sup> reported a doping approach to tailor the optoelectronic properties of HTL by spin-coating an acetonitrile solution of 2,2'-(perfluoronaphthalene-2,6-diyldene)dimalononitrile (F6TCNNQ) onto the NiO<sub>x</sub>. The F6TCNNQ doping increased Fermi level of NiO<sub>x</sub> HTLs from -4.63 eV to -5.07 eV, and reduced the valence band maximum from 0.58 eV to 0.29 eV, leading to an increase in champion PCE of CsFAMA mixed cations and MAPbI<sub>3</sub>-based devices to 20.86% and 19.75%, respectively. Alkali halide were introduced as interlayer between HTL/PVK to manipulate the properties of PVK and improve the performance of inverted PSCs. Chen et al.<sup>[206]</sup> reported a facial strategy for suppressing interfacial recombination by alkali chloride interface modification of NiO<sub>x</sub> HTL surface. They revealed that alkali chloride interface modification results in improved properties of CsFAMA-based PVK and reduced interfacial recombination owing to the interface contact healing by halide elements. Finally, this KCl-doping strategy led to a significant improvement in the  $V_{oc}$  from 1.07 eV for pristine NiO<sub>x</sub> to 1.15 eV for KCl-treated NiO<sub>x</sub>, resulting in a

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power conversion efficiency approaching 21%. Moreover, the PVK deposited on the alkali halide modified NiO<sub>x</sub> layer exhibited lower rates of ion migration, showing improved device stability.

In conclusion, we have shown that halides compounds are also employed at the interface of ETL/PVK and PVK/HTL, suppressing the defects of ETL and PVK, improving the charge transfer and reducing the charge recombination. Meanwhile, modification of interfaces of PSCs improves the PVK crystallinity, energy-level alignment and the stabilization of the PSCs against UV-light, humidity and oxygen degrading agents.

## Conclusion and Outlook

PSCs have attracted special attentions due to their excellent power conversion efficiency, low cost and great promise for the future of solar energy. The best PSC has already achieved a certified PCE of 25.5% after an unprecedented rapid performance rise. However, high requirement with respect to large area high efficiency devices and stability are still the challenge and focuses major efforts on the PSC research. The primary requirement to achieve high efficiency and stable devices is to understand in great depth the optoelectronic loss mechanism for the devices and the degradation mechanism of individual layers in PSCs. Although various mechanisms still need to be explored, the bulk and surface trap states and large numbers of grain boundaries are the main reasons reported up to now affecting the performances of PSCs. To overcome the bulk and surface trap states, one of the ways is additive/compositional engineering in the PVK bulk. On the other hand, interfacial modifications to form proper capping/buffer layer or charge transport layer are considered as effective strategies to improve stability and efficiency of PSCs.

Herein, we have given an in-depth review of the various strategies and halide/pseudo-halide compounds employed as additives for films and interfaces quality improvements. If many experimental works have been implemented and analyzed throughout the paper, the exact role of these additive should be rationalized. Developing modelling and theoretical works could help the understanding.

Halide additives-engineered PVKs have been proved as an effective approach to passivate the defects in the PVK bulk and interfaces, reducing energy loss and improving the performance of PSCs. However, complete understanding of passivation mechanism and PVK crystallization process has yet to be totally resolved, due to the limited characterization technique for the defect types and density in different PVK

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materials. It renders difficult to guide the design of efficient additives and achieve universal efficient passivation strategy. Thus, a further understanding of passivation mechanism through characterizing the traps types and concentration at the PVK surface and grain boundaries, as well as revealing the role of additives on the PVK crystallization process will be crucial for highly efficient and stable PSCs. New techniques to understand the crystallization mechanism and growth direction of the crystals in the layer must be developed. Developing double (or more) mixed halide additive is of high interest and must be developed to achieve multiple and synergistic beneficial effects (phase purity, better crystallinity, grain boundaries reduction, defect passivation, monolithic morphology...).

Concerning the PVK surface treatment by halide compounds, it will be necessary to better control the properties of the produced interfacial layers including their thickness and their chemical composition. An in-depth understanding of why the treatment with a halide compound is beneficial with a PVK and not with another is required and give an important research direction for future works. Halide additives in charge carrier layers have mainly been used in inorganic materials. A further understanding if their effects are bulk or near-interface related is still necessary and give another important research direction for the future. For the testing of the device stability, standardized aging tests should be implemented on the perovskites and devices implementing halide/pseudo-halide additives. The objective should be to meet stability standards of IEC61215:2016 qualification tests, for instance, a target that would necessitate to encapsulate tightly and efficiently the solar cells.

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Fei Cheng received her master's degree from Guangzhou Institute of Chemistry, University of Chinese Academy of Sciences in 2019. She is a current Ph.D. student under the supervision of Prof. Thierry Pauporté in Chimie ParisTech-PSL University. Her research interests are focused on development of efficient and stable perovskite solar cells.



Dr. Jie Zhang is currently an assistant professor in the School of Chemistry and Chemical Engineering at the South China University of Technology. She received her M. Sc. and Ph. D. degree at the South China University of Technology and Chimie ParisTech in 2012 and 2015, respectively. Her interests concentrate on the synthesis of novel photo-functional materials and perovskite solar cells, including photochromic materials, low-dimensional perovskites and device engineering for perovskite solar cells.



Prof. Thierry Pauporté is director of research at the Centre National de la Recherche Scientifique (CNRS) in France and works at Chimie-Paristech-PSL University. He is graduated in Chemistry from the École Normale Supérieure de Lyon. He received his Ph.D. in physical chemistry from Montpellier II University, France, in 1995. He works on the synthesis, characterization and understanding of fundamental chemical and physical properties of oxide and halide perovskite films and nanostructures. The applications of these materials and structures include light emitting diodes, perovskite solar cells, dye-sensitized solar cells, nanosensors,

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## Table of Content

Progresses made on the employment of halide and pseudo-halide additives in organo-metal perovskite solar cells are reviewed. Their function in morphology adjusting, phase stabilizing, energy-level adjusting, trap state passivation and hysteresis elimination are detailed. A deep understanding of the relationship between halide/pseudohalide additive and the improved properties of perovskite solar cell is presented.

