Doping and alloying for improved perovskite solar cells

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Doping and/or alloying in the various layers in perovskite solar cells (PSCs) is playing a key role in the success of this new photovoltaic (PV) technology. Here we present a brief review of doping and alloying approaches used to enhance the efficacy of the hybrid organic–inorganic perovskite (HOIP) layer, the electron-transporting layer (ETL), the hole-transporting layer (HTL), and the electrode layers in PSCs. While the effectiveness of these approaches is beyond doubt, the fundamental understanding of doping and alloying in the majority of the cases is lacking. This presents vast research opportunities in elucidating the roles of doping and alloying, and the rational design and implementation of these approaches for enhanced PSCs performance.

1. Introduction

We are witnessing the emergence of perovskite solar cells (PSCs) as a new generation photovoltaic (PV) technology,1–6 where the power conversion efficiency (PCEs) of PSCs have shot up to >22% in an unprecedentedly short period of time of seven years.1 PSCs employ a group of hybrid organic–inorganic perovskite (HOIP) materials as light absorbers, with the general formula of ABX₃ (see Fig. 1), where A = CH₃NH₃⁺ (methylammonium or MA⁺), HC(NH₂)₂⁺ (formamidinium or FA⁺), or Cs⁺; B = Pb²⁺ or Sn²⁺; and X = I⁻, Br⁻, or Cl⁻.⁶ Amongst these compounds, methylammonium lead triiodide (CH₃NH₃PbI₃ or MAPbI₃) HOIP is the most widely studied composition. Although the synthesis and basic properties of MAPbI₃ were studied in the early 1990s,⁷ Kojima et al.⁸ were the first to demonstrate the use of the MAPbI₃ as the ‘dye’ in liquid-junction PSCs, a derivative of dye-sensitized solar cells (DSSCs). However, the performance of such liquid-junction PSCs degraded rapidly due to the dissolution of these HOIP ‘dyes’ in the liquid electrolyte.¹⁰ In order to resolve this issue, in 2012, Kim et al.¹⁰ replaced the liquid electrolyte with solid-state hole-transporting materials, and fabricated all-solid-state PSCs with PCEs up to 9.3%. In parallel, Lee et al.¹¹ invented a novel mesosuperstructured solar cell, where an insulating mesoporous Al₂O₃ scaffold was used to replace the conventional electron-transporting mesoporous TiO₂ scaffold. A surprising 10.2% PCE was achieved in these PSCs.¹¹ This invention eventually led to the emergence of planar-structured PSCs, as the insulating mesoporous Al₂O₃ layer did not appear to play an actual role in the solar cell operation. To date, extensive effort has gone into optimizing the solar cell structure,¹¹,¹² and it appears that the mesoscopic–planar hybrid PSC with both a mesoporous TiO₂/HOIP composite layer and a planar HOIP capping layer is the most efficient embodiment, as it combines the merits of both mesoscopic and planar-junction PSCs.¹³,¹⁴

While optimization of PSCs architecture has played a key role in the early stages of PSCs development, there has been a surge of interest in the compositional tailoring of the PSC device components, which is expected to further the advance of PSCs technology in terms of PCE, stability, toxicity, etc. As seen in Fig. 2, a typical PSC consists of a HOIP absorber layer, an electron-transporting layer (ETL), a hole-transporting layer (HTL), and the electrode contacts.¹³ Under illumination, the light is absorbed by the HOIP layer, where charge carriers (electrons and holes) are generated. These photo-generated

Fig. 1 (A) Schematic crystal structure of HOIPs with typical A, B, and X site ions. (B) Methylammonium (MA) and formamidinium (FA) molecular cations.

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2. Alloying and doping in ABX₃ HOIPs

As per the above criteria for distinguishing doping and alloying, most studies in the literature in the area of compositional tailoring of the HOIP absorbers are focused on alloying, where alloys can be formed by substituting A, B, and X sites with their corresponding elemental or molecular analogues in the ABX₃ perovskite crystal structure.

2.1. A-site alloying in ABX₃ HOIPs

The most popular MAPbI₃ HOIP has a bandgap of ≈1.55 eV.²⁻⁴ To further reduce the bandgap, the FA⁺ cation (ionic radius: ~2.2 Å),²³ which is slightly larger than the MA⁺ cation (ionic radius: ~1.8 Å),²¹ can be incorporated into the MAPbI₃ perovskite structure, forming mixed-organic-cation HOIP alloys MAₓFA₁₋ₓPbI₃ (x ranging from 0 to 1) with extended absorption into the near-infrared (IR) region of the solar spectrum (Fig. 3A). Pellet et al.¹⁴ were the first to investigate the properties and performance of the MAₓFA₁₋ₓPbI₃ HOIP alloys in mesoscopic PSCs. In that study, MAₓFA₁₋ₓPbI₃ HOIPs were formed via the classic ‘dipping’ reaction of pre-deposited PbI₂ mesoscopic films with the tailored MAₓFA₁₋ₓPbI₃ solution in isopropanol.¹⁴ They showed that the MA₀.₆FA₀.₄PbI₃ composition alloy exhibited the best overall PSC performance (Fig. 3B), with an extended absorption edge at ~810 nm, which is close to that of pure FAPbI₃ HOIP.²⁴ Several later studies have implied that the superior performance of PSCs based on MAₓFA₁₋ₓPbI₃ alloys compared to pure FAPbI₃ may also be related to the phase instability of pure FAPbI₃ HOIP in the ambient.¹₅,²⁵ In fact, FAPbI₃ has two possible polymorphs at room temperature, the ‘black’ perovskite phase (z-FAPbI₃, space group Pm3m [ref. 26]) and the ‘yellow’ non-perovskite phase (δ-FAPbI₃, space group P6₃mc [ref. 26]). In the ambient, the ‘yellow’ δ-FAPbI₃ can form easily via a facile α → δ phase transition²⁶ or as a byproduct associated with the crystallization of the FAPbI₃ HOIP.²⁸,³⁰ However, interestingly, the incorporation of MA⁺ into the FAPbI₃ perovskite structure results in much more stable HOIP phases. This idea was first proposed by Jeon et al.¹² who prepared stable PSCs based on (MAPbBr₃)₀.₅(FAPbI₃)₀.₅ HOIP composition, and achieved a record (at that time) certified PCE of 16.2%. Regardless of the additional Br alloying (discussed below) in that work, the alloying of MA⁺ and FA⁺ is expected to play a major role in stabilizing the perovskite phase, which was further studied by Binek et al.²⁶ As shown in Fig. 3C and 3D, incorporation of MA⁺ cation favors the solution crystallization of high-purity perovskite phases. It is hypothesized that the higher dipole of MA⁺ cation has stronger interaction with the [PbI₆] octahedral cage, which stabilizes the perovskite structure as shown in Fig. 3E. Owing to the combined merits of extended absorption and enhanced ambient stability, MAₓFA₁₋ₓPbI₃ HOIP alloys have been studied extensively,²⁶⁻²⁸ and various fabrication techniques have been developed in order to realize their full potential in PSCs. For example, Liu et al.³¹ prepared high-quality MAₓFA₁₋ₓPbI₃ HOIP thin films via a two-step reaction of MAI with an (FAI)ₓ₋₁PbI₃ intermediate complex. Deng et al.³² developed a ‘doctor-blading’ process for scalable deposition of MAₓFA₁₋ₓPbI₃ HOIP thin films. High performance and stability in the resulting PSCs were achieved, which are attributed to the intrinsic merits and improved grain morphologies of MAₓFA₁₋ₓPbI₃ HOIP alloys.³²–³⁴
Similar to MA⁺, elemental Cs⁺ cation (ionic radius: 1.67 Å)\textsuperscript{35–37} has also shown exceptional promise as an A-site alloying candidate for stabilizing FAPbI\textsubscript{3} perovskite. Lee et al.\textsuperscript{35} first reported Cs\textsubscript{x}FA\textsubscript{1−x}PbI\textsubscript{3} HOIP alloys and hypothesized that the substitution of FA⁺ by Cs⁺ induces the contraction of the cubo-octahedral volume, and thereby enhances (FA⁺−I⁻) interaction, which stabilizes the perovskite structure. They showed that substitution of 10% of FA⁺ cations by Cs⁺ enhances the photo-stability and the moisture-tolerance of the PSCs significantly, while increasing the PCE from 14.9% to 16.5%. A similar observation was later reported by Yi et al.,\textsuperscript{36} where they performed first-principles calculations to elucidate such remarkable stabilization behavior. As shown in Fig. 4, the entropic gains, together with the small internal energy input, favor the formation of α-phase Cs\textsubscript{x}FA\textsubscript{1−x}PbI\textsubscript{3} compounds with a stable perovskite structure over the δ-phase. The enhanced stability of Cs\textsubscript{x}FA\textsubscript{1−x}PbI\textsubscript{3} HOIPs was also explained by Li et al.\textsuperscript{37} using empirical Goldschmidt tolerance factor (\(t\)) considerations. It was shown that the calculated \(t\) for FAPbI\textsubscript{3} is \(t > 1\), while \(t < 0.8\) for CsPbI\textsubscript{3}. Through alloying of large-\(t\) FAPbI\textsubscript{3} and small-\(t\) CsPbI\textsubscript{3}, \(t\) can be tuned to between 0.8 and 1.0 in Cs\textsubscript{x}FA\textsubscript{1−x}PbI\textsubscript{3} compounds, which favors their existence in stable perovskite structure. However, although these studies have claimed the successful alloying of Cs⁺ and FA⁺ in the perovskite structure, it is not clear whether Cs⁺ is indeed incorporated into the perovskite crystal structure. Thus, the unambiguous determination of the exact location of Cs⁺ in Cs\textsubscript{x}FA\textsubscript{1−x}PbI\textsubscript{3} HOIPs would be very important for understanding the underlying mechanism of Cs⁺–FA⁺ alloying-induced phase stabilization.

### 2.2. B-site alloying in ABX\textsubscript{3} HOIPs

B-site alloying is primarily adopted to address the toxicity of HOIP materials. To date, the most efficient PSCs employ lead (Pb)-based HOIPs (FAPbI\textsubscript{3}, MAPbI\textsubscript{3}, etc.) that contain...
a significant fraction (>30 wt%) of Pb. This raises toxicity concerns for manufacturing, deployment, and disposal of future PSCs. To address this issue, tin (Sn), as an elemental analogue of Pb, is chosen to replace the Pb in HOIPs. However, several studies have shown that the use of MASnI₃ light absorbers in PSCs results in significantly inferior performance (<10% PCEs) compared to Pb-based PSCs, primarily due to the metallic nature of MASnI₃. In this context, an interesting strategy is to use MAPbₓSn₁₋ₓI₃ alloys to reduce the amount of Pb contained within PSCs, while maintaining high PSC performance. It is also worth noting that, while Sn is less toxic than Pb, Babaíst et al. have shown that the strong acidification of Sn-based perovskites can also cause environmental concerns.

In this context, Stoumpos et al. experimentally confirmed that MAPbₓSn₁₋ₓI₃ HOIP alloys with the 3D perovskite structure can form a mixture of MAPbI₃ and MASnI₃ via either solid reaction or solution synthesis. Changing the x value results in the tuning of the optical absorption of these HOIPs, as shown in Fig. 5A. Interestingly, as seen in Fig. 5B, the bandgap change with x does not follow a linear trend (Vegard’s law) in MAPbₓSn₁₋ₓI₃, but instead an anomalous bandgap behavior is observed. It appears that a HOIP composition of MAPbₓSn₁₋ₓI₃ prepared from solution route has the lowest bandgap of 1.17 eV, compared to 1.55 eV for MAPbI₃ and 1.30 eV for MASnI₃. PSCs using MAPbₓSn₁₋ₓI₃ HOIP as the light absorber were also reported by Hao et al. and Ogomi et al. The edges of the external quantum efficiency (EQE) spectra from these PSCs were found to extend to 1060 nm wavelength, owing to the optimized bandgap. However, in contrast to the experimental observations, density functional theory (DFT) calculations by Ju et al. and by Mosconi et al. revealed that the calculated bandgaps of MAPbₓSn₁₋ₓI₃ HOIPs are proportional to the x value. Such inconsistency between experiment and theory could be due to the variation in the real crystal symmetry of perovskites with different x values. Note that the crystal structure of pure MAPbI₃ perovskite is tetragonal [space group I4/mcm], whereas that of pure MASnI₃ is cubic [space group Pm₃m] at room temperature. Therefore, more careful analyses of the crystal structures of MAPbₓSn₁₋ₓI₃ HOIP alloys, and more refined theoretical models, are needed to elucidate the origin of this anomalous bandgap behavior. Nevertheless, in the case of MAPbₓSn₁₋ₓBrₓ, Mancini et al. indeed observed a linear trend of the bandgap, with increasing Sn content, from 2.20 eV (x = 0) to 1.33 eV (x = 1), which can be related to the fact that MAPbBr₃ and MASnBr₃ exhibit the same cubic symmetry. In addition to the bandgap-tuning effect, DFT calculations by Mosconi et al. also revealed that mixed Sn–Pb HOIP alloys show more balanced electron and hole effective-mass values compared to single-metal-cation HOIPs. In this regard, although PCEs of PSCs based on Pb–Sn HOIP alloys are still lower than those based on Pb alone, these alloys are promising for their reduced toxicity and extended absorption, as well as enhanced charge-transport properties.

2.3. X-site alloying in ABX₃ HOIPs

Since the halogen ion plays a profound role in determining the bandgap of halide HOIPs, alloying of smaller cation halides (Br⁻) into lead iodide HOIPs (MAPbI₃, MASnI₃, FAPbI₃, etc.) allows bandgap tuning in a wide range of 1.45 to 2.3 eV. Since the time Noh et al. investigated the application of mixed I–Br HOIPs (MAPbIₓBr₁₋ₓ) for enabling the color management of PSCs (Fig. 6A and B), several studies on the crystallization and physical properties (photovoltaic, luminescent, etc.) of these HOIPs have been reported. In particular, MAPbIₓBr₁₋ₓ (x = 0.6–1.0) HOIPs have bandgaps of 1.7–1.8 eV, which hold unprecedented promise in the application as top-cell, in conjunction with low-bandgap inorganic bottom-cell based on crystalline Si or copper–indium–gallium–selenide (CIGS), in tandem devices. However, it has been shown that these MAPbIₓBr₁₋ₓ (x > 0.6) HOIPs show phase segregation under illumination, resulting in the formation of I-rich and Br-rich regions. Such photo-induced phase segregation behavior may limit the performance of the corresponding PSCs, as the open-circuit voltage (V_OC) can be pinned by the segregated I-rich phase. Also, a randomly distributed low-bandgap phase in the film acts as charge traps that reduce the photocurrent in PSCs. Similar photo-instability issue may occur in the FAPbIₓBr₁₋ₓ as
well.\textsuperscript{34} Furthermore, it is claimed that partial substitution of I\textsuperscript{–} with Br\textsuperscript{–} may enhance the moisture tolerance of mixed-halide HOIPs.\textsuperscript{35} However, in a conflicting report it was shown that the introduction of Br\textsuperscript{–} actually stresses the perovskite structure and accelerates its degradation.\textsuperscript{36} Besides Br\textsuperscript{–}, Cl\textsuperscript{–} has also been suggested as an alloying anion for MAPbI\textsubscript{3} HOIP in the early stage of PSCs development,\textsuperscript{37} but, this issue is still controversial, which is discussed in Section 2.5.

### 2.4. Dual-site or triple-site alloying in ABX\textsubscript{3} HOIPs

As discussed above, A-, B-, and X-site alloying strategies are generally adopted for improving different aspects of PSCs. Thus, it is possible to combine two or three of them simultaneously in order to achieve multiple goals. For example, as mentioned earlier, the photo-stability of the promising mixed-halide HOIP alloys (MAPb\textsubscript{1−x}Br\textsubscript{x} or FAPb\textsubscript{1−x}Br\textsubscript{x}) is a concern, and, therefore, further A-site alloying is adopted to alleviate this issue. It appears that such dual-site compositional engineering could lead to the formation of stable mixed-halide HOIPs with continuous bandgaps/colors, as seen in Fig. 7A and 7B. McMeekin et al.\textsuperscript{38} showed that the photoluminescence (PL) emission of the dual-site perovskite alloy FA\textsubscript{0.85}MA\textsubscript{0.15}Pb\textsubscript{1−x}Br\textsubscript{x} HOIP thin films does not red-shift under monochromatic irradiance of much higher irradiance of 5 W cm\textsuperscript{–2} after 240 seconds, whereas obvious red-shift is observed in thin films made of neat FA-based mixed-halide HOIPs (Fig. 7C). Furthermore, elemental substitution at each site in ABX\textsubscript{3} structure may have a combined effect on the intrinsic properties as well as the crystallization process of the HOIP materials. In this context, there is a clear trend towards using these dual-site HOIP alloys with more complicated compositions (e.g. FA\textsubscript{0.8}MA\textsubscript{0.2}Pb\textsubscript{1−x}Br\textsubscript{x} [ref. 13 and 56], Cs\textsubscript{0.17}FA\textsubscript{0.83}Pb\textsubscript{1−x}Br\textsubscript{x} [ref. 59], FA\textsubscript{x}MA\textsubscript{1−x}Pb\textsubscript{1−y}Br\textsubscript{y} [ref. 60]), in the PSCs to achieve maximum PSC performance. However, the reasons why these particular compositions result in the enhancement in the PSC performance are far from well-understood, which can be an important subject for future research in PSCs. Also, although a HOIP alloy with simultaneously mixed compositions at all the three sites (A, B, and X) has not been reported, such triple-site alloys might open up new opportunities for higher-performance PSCs.

### 2.5. Doping in ABX\textsubscript{3} HOIPs

Compared with the extensive studies on alloying of HOIPs, there have been relatively fewer studies on doping of HOIP, and they appear to be more controversial. One of the most popular topics still under debate is the effect of chlorine (Cl\textsuperscript{–}). In 2012, Lee et al.\textsuperscript{2} reported that the mixed-halide HOIP ‘MAPb\textsubscript{1−x}Cl\textsubscript{x}’ is an efficient light absorber in PSCs. But later on, it was recognized that single-phase ‘MAPb\textsubscript{1−x}Cl\textsubscript{x}’ alloy does not exist, and, thus, the ‘MAPb\textsubscript{1−x}Cl\textsubscript{x}’ nomenclature was adopted as the value of x is not known.\textsuperscript{41} One hypothesis is that Cl\textsuperscript{–} may work as a dopant with very little concentration in MAPb\textsubscript{3}, which can only be detected by high-resolution analytical characterization tools.\textsuperscript{42–44} However, Cl\textsuperscript{–} has been found to play a significant role in the solution crystallization and grain growth of MAPb\textsubscript{3}.\textsuperscript{65–67} Thus, it still is a mystery whether the slight amount of remnant Cl\textsuperscript{–} in

\[E_g(x) = 1.57 + 0.39x + 0.33x^2\]
Pb(I0.6Br0.4)3 HOIP alloys as a function of laser excitation time (reprinted with permission from ref. 54).

Another type of popular proposed dopants is molecular ions. Cl\textsuperscript{−} et al. 71 explored possible doping by monovalent cations with ionic radii similar to that of Pb\textsuperscript{2+} (e.g. Cu\textsuperscript{+}, Na\textsuperscript{+}, etc.), where they concluded that such doping has significant effect on the absorption and hole mobilities compared to undoped MAPbI\textsubscript{3} HOIP. Abdelhady et al. 68 reported trivalent-dopant incorporation in HOIP crystals and achieved four orders-of-magnitude enhancement in the electrical conductivity, and a change in the sign of majority charge carriers via Bi\textsuperscript{3+} incorporation. Another type of popular proposed dopants is molecular ions. Mei et al. 73 and Chen et al. 69 respectively, reported doping of amino-acid cation and BF\textsubscript{4}− anion for the enhancement of electronic properties and photovoltaic performance of HOIPs in HTL-free mesoscopic PSCs. Pseudohalide cations such as SCN\textsuperscript{−} are also studied as possible dopant candidates for HOIPs. 70,71 But, again, the exact roles of these proposed ‘dopants’ need to be further elucidated and separated, as the effect of these ‘dopants’ in the solution crystallization of HOIPs can be usually profound. 74 Furthermore, there is no available information indicating that the reported doping in the HOIP is either p-type or n-type. Meanwhile, it is interesting that Yin et al. 75 and Wang et al. 76 showed experimentally and theoretically, respectively, that HOIPs may be possibly self-doped as a result of the manipulation of crystal defects.

3. Doping in ETLs

ETLs in PSCs are broadly classified into two categories: inorganic and organic. TiO\textsubscript{2} and C61-butyric acid methyl ester (PCBM) are the most commonly used inorganic and organic ETLs, respectively. 77 Neat ETL materials are limited in their electron-transporting characteristics (electron mobility and conductivity) due to their polycrystalline or semi-crystalline nature. In particular, TiO\textsubscript{2} ETL materials synthesized at low temperatures have even poorer electronic properties. In this context, incorporation of dopants or additives into TiO\textsubscript{2} and PCBM becomes necessary to match the excellent electronic properties of HOIP absorber materials 78 in order to optimize the PSC performance.

3.1. Doping in TiO\textsubscript{2} ETLs

Doping of TiO\textsubscript{2} ETLs (which also includes the TiO\textsubscript{2} mesoporous layer) has been studied extensively in the context of DSSCs. 79–82 In TiO\textsubscript{2}, both cationic and anionic dopants can be used. The former are mostly metals (Li, Mg, Zr, Nb, etc.) whereas the latter are non-metals (C, N, etc.). 79 Cationic dopants are expected to affect the conduction band (CB) and the valence band (VB), whereas anionic dopants are expected to influence the Fermi level (E\textsubscript{F}), with profound impact on the electron injection/transport in the PSC devices. The mechanisms of doping in TiO\textsubscript{2} have been reviewed extensively by Roose et al. 79 and is summarized here. As shown in Fig. 8A, in pristine TiO\textsubscript{2}, electrons are transported by hopping from one shallow trap to another shallow trap. 79 The shallow-trap density influences electron transport rate, and, thus, the short-circuit current density (J\textsubscript{SC}) in solar cells. 79 But, deep traps can trap electrons permanently, and act as recombination sites, affecting V\textsubscript{OC}. 79 In some cases, doping decreases the deep-traps density and results
in an upward shift of $E_F$, both of which contribute to an increase in $V_{OC}$. Note that $V_{OC}$ is also defined as the difference between $E_F$ of TiO$_2$ and the HTL. However, since CB also shifts towards lowest unoccupied molecular orbitals (LUMO) of the absorber, the driving force for electron injection is lowered. This combined with a decreased trap density, and the related electron transport, lowers $J_{SC}$. In some other cases, doping contributes to the formation of deep traps, resulting into the downward shift of the CB and $E_F$ (reprinted with permission from ref. 79). (B) The anatase TiO$_2$ unit cell, with Ti atoms in grey and O atoms in red (reprinted with permission from ref. 79). (C) Schematic illustration of Al-doping in TiO$_2$ for passivation of deep traps (reprinted with permission from ref. 90). (D) Schematic illustration of a PSC using Nb-doped TiO$_2$ ETL and (Mg, Li)-doped NiO HTL (reprinted with permission from ref. 89).

Fig. 8  (A) Schematic illustration showing the effect of doping on the CB and $E_F$ of TiO$_2$. The doping-induced states are shown in red. Left: In pristine TiO$_2$, electrons are transported by 'hopping' from one shallow trap to another shallow trap. Center: In some cases, doping decreases the deep trap density and results in an upward shift of $E_F$ and conduction band. Right: In some other cases, doping contributes to the formation of deep traps, resulted into the downward shift of the CB and $E_F$ (reprinted with permission from ref. 79). (B) The anatase TiO$_2$ unit cell, with Ti atoms in grey and O atoms in red (reprinted with permission from ref. 79). (C) Schematic illustration of Al-doping in TiO$_2$ for passivation of deep traps (reprinted with permission from ref. 90). (D) Schematic illustration of a PSC using Nb-doped TiO$_2$ ETL and (Mg, Li)-doped NiO HTL (reprinted with permission from ref. 89).
shows the typical PSC structure made by Chen et al. using a Nb-doped TiO₂ ETL, where the PCE of PSC reached >15% (certified), for the first time, in an active cell area >1 cm², with doping playing a key role.

Doping in TiO₂ can also alleviate hysteresis and stability issues in PSCs using TiO₂ ETLs; it has been suggested that this is related to the intrinsic oxygen vacancies in the anatase TiO₂ (Fig. 8B). The oxygen vacancies can act as deep trap states in TiO₂. Through incorporation of dopants such as Al³⁺, these trap states can be effectively reduced as shown in Fig. 8C, ameliorating the PSC degradation issue. Nagaoka et al. and Giorlando et al. showed that the hysteresis of PSCs is also significantly reduced by passivation of TiO₂ surface traps via cationic doping.

Doping in TiO₂ ETLs may have other non-electronic effects in the PSCs. For example, it is observed that Y-doping also affects the surface properties of TiO₂, which improves the crystallization of HOIPs on top of the TiO₂. Overall, there are vast research opportunities in studying doping effect in TiO₂ for PSCs and understanding the underlying mechanisms, as well as developing effective doping strategies in TiO₂ via various synthetic routes. It is expected that the lessons learned from DSSCs research in the past two decades in this area will have significant impact on the progress of PSCs.

3.2. Doping in fullerene ETLs

The basic mechanism of doping in organic materials is similar to that in inorganic semiconductors (e.g. TiO₂). As shown in Fig. 9A, dopants are needed to donate electrons to LUMO states in inorganic semiconductors does not work for organic semiconductors. Moreover, unlike doping in inorganic materials, insights into the doping of organic semiconductors are far less developed, which is due to the fact that the widely used hydrogen model for inorganic semiconductors does not work for organic semiconductors. Nevertheless, the past studies have established various empirical doping rules in the field of organic PVs, which can be adopted for the development of PSCs.

To enhance the electrical properties of the fullerene ETLs, Kim et al. reported 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzoimidazole (DMBI) as an effective n-dopant. They showed that the electrical conductivity of the DMBI-doped PCBM film (6.1 × 10⁻⁵ S cm⁻¹) is four orders-of-magnitude higher than that of the pristine PCBM film (3.8 × 10⁻⁹ S cm⁻¹), and the Eₚ level up-shifts after DMBI-doping. Correspondingly, PSCs using DMBI-doped PCBM exhibit higher PCEs with remarkably higher Jₚ⁰. Similarly, Kuang et al. introduced graphdiyne (GD) into the PCBM layer in PSCs, which enhances the electrical conductivity, electron mobility, and charge extraction ability in the ETL layer, owing to the delocalized π-systems of GD material (shown schematically in Fig. 9B). The corresponding PSCs has a ~30% increase in overall PCEs (from 10.8% to 13.9%) after GD ‘doping’. Another interesting study by Bai et al. showed that MAI, an ingredient in the HOIP solution precursor, could be also serve as a good dopant for PCBM, since the halide ions are good electron donors.

It is noteworthy that dopants for PCBM are usually incorporated through one-step solution processing, and, thus, the addition of dopants in the PCBM solution may also have beneficial effects on the morphological development of PCBM layers from the solution. It is shown that dopants such as GD and oleamide can improve the coverage and compactness of the solution-processed PCBM ETLs, contributing to the performance enhancements in PSCs. Therefore, the use of a dopant contributing to both, the intrinsic electronic properties and the morphologies of PCBM layers, can possibly lead to a further boost in the performance of PSCs.

4. Doping in HTLs

Like ETLs, HTLs can also be classified into two groups: organic and inorganic. So far, the most widely used HTL in PSCs is organic Spiro-OMeTAD molecules (the molecular structure is shown in Fig. 9C). However, due to the low hole mobility (~4 × 10⁻⁹ cm² V⁻¹ s⁻¹) of the solution-processed Spiro-MeOTAD layer as result of a lack of molecular ordering, neat Spiro-OMeTAD is inadequate for achieving high PCEs in PSCs. In the past, a variety of materials have been reported as p-type dopants to enhance the electronic properties of the Spiro-OMeTAD layer for improved performance of solid-state DSSCs (see example in Fig. 9D). These dopants include SnCl₄, (p-BrC₆H₄)₃NSbCl₄ and tris(2-(1H-pyrazol-1-yl)pyridine)cobalt(m). Lithium-bis(trifluoromethylsulfonyl)-imide (Li-TFSI) salt has also been reported to enhance significantly the hole mobility of Spiro-OMeTAD, as Li⁺ can react with oxygen and Spiro-OMeTAD to facilitate the formation of oxidized Spiro-OMeTAD, while the large anion TFSI stabilizes the oxidized Spiro-OMeTAD. For PSCs, the success of Li-TFSI dopant has been confirmed by the fact that most of the best PSCs employ a Spiro-OMeTAD layer with Li-TFSI doping. However, there are also issues associated with Li-TFSI due to its hydrophilic nature, which absorbs moisture from the ambient and degrades the PSCs. Therefore, other possible dopants have been explored. For example, Zhang et al. reported an ionic liquid N-butyl-N’(4-pyridylheptyl)imidazolium bis(trifluoro-methane)sulfonimide (BuPyIm-TFSI) in Spiro-OMeTAD, which can enhance both electronic properties and environmental stability.

Besides the most popular Spiro-OMeTAD HTL, a wide range of p-type semiconducting polymers are good HTL candidates for PSCs. Compared with Spiro-OMeTAD, these polymers usually have even poorer intrinsic electrical properties, in which case Li-TFSI is also added for their better function in the PSCs. However, Heo et al. suggested that those amine-moiety-free polymers do not form complexes with TFSI, where true chemical doping does not occur, and the significantly enhanced conductivity is due to the additional hole conduction mediated by Li-TFSI. Based on a similar mechanism, Xiao et al. have shown that GD can also be a promising ‘dopant’ for polymer HTLs. For those organic HTLs generally used in inverted-structure PSCs, less attention has been paid to doping, because even the applied HTL is already very conductive (e.g. poly(3,4-ethylenedioxythiophene) polystyrene sulfonate or PEDOT:PSS), or the thickness of the HTL can be small enough.
so that its conductivity does not limit the photocurrent extraction (e.g. poly(triaryl amine) poly[bis(4-phenyl)(2,4,6-trimethyl-phenyl)amine] or PTAA). For the latter, when a thicker PTAA layer is needed to smooth-out the substrate, doping of PTAA has also been explored with popular acceptors such as F4-TCNQ.

Inorganic HTL materials, in particular NiO, have been studied extensively considering its higher stability and lower cost.\textsuperscript{115-117} Similar to TiO\textsubscript{2}, several metal ions can be used as dopants in NiO for enhancing its hole conduction.\textsuperscript{118-121} In a recent PSC study, Chen \textit{et al.}\textsuperscript{89} showed that through co-doping of NiO by Li and Mg (Fig. 8D), the conductivity can be increased to $2.32 \times 10^{-3} \text{ S cm}^{-1}$, from $0.166 \times 10^{-3} \text{ S cm}^{-1}$ for an undoped NiO thin film. Also, Jung \textit{et al.}\textsuperscript{122} and Kim \textit{et al.}\textsuperscript{123} showed that Cu-doped NiO thin films can be an efficient HTL material for PSCs, highlighting the importance of doping in inorganic HTL materials. Like NiO, doping in other inorganic HTL materials such as CuI\textsuperscript{124} and CuSCN\textsuperscript{125} may have similar positive effects on PSCs performance, which has not been widely studied.

5. Doping in electrodes

At least one of the electrodes in PSCs needs to be transparent to allow sunlight into the device. Here doped transparent conductive oxide (TCO) are widely used, including fluorinedoped tin oxide (FTO) and indium-doped tin oxide (ITO). These two are commercially available, and are used as-received without further dopant engineering. However, the doping characteristics in this electrode could have several important implications on the PSC performance. First, the current FTO or ITO technology could be advanced further. The sheet resistance of commercially available FTO or ITO adds to the series resistance in PSCs, leading to a drop in the fill factor (FF) as the active area of the PSC increases.\textsuperscript{126} Therefore, to explore more superior doping strategies to achieve highly transparent, conductive TCOs can play an important role in the fabrication of large-area PSC panels. Second, doping affects the $E_r$ of the electrode, where the interfacial charge transfer characteristics can be influenced. Third, doping can also be used to engineer...
the surface properties of TCOs, which can influence the growth of the ETL or HTL on top of the TCO layer.

6. Outlook

It is envisioned that future large-area PSCs are solution-processed at low temperatures, are high efficiency, and are highly durable. They are also expected to have various functionalities such as semitransparency, flexibility, and with tunable colors. Doping and alloying are two extremely important compositional engineering methods for meeting these desirable PSC characteristics. Indeed most recently reported state-of-the-art PSCs consist of layers that are doped and/or alloyed.8,11,12,18 Thus, each functional layer in the future commercialized PSCs is likely to be doped and/or alloyed.

Although various doping and/or alloying strategies have been demonstrated to improve different aspects of PSCs in the literature, several challenges still remain in the fundamental understanding of the underlying mechanisms. First, the phase-homogeneity of these doped and/or alloyed layers (HOIP, HTL, ETL, and electrodes) awaits elucidation using high-spatial-resolution, high-sensitivity analytical characterization methods. Second, the exact role of doping and/or alloying in PSCs is difficult to elucidate because doping and/or alloying can influence the microstructural development of these solution-processed materials, making it difficult to separate the different effects. Third, in the most important case of doping in HOIPs, many of studies in the literature have not justified the exact doping type (p or n), although the ‘doping’ effect has been claimed. This may be related to the fact that the p/n nature of PSCs themselves is still being debated. We believe that further advances in these fundamental aspects will point to clearer directions in the exploration of the most effective doping and/or alloying approaches that are important for the development of next-generation PSCs.

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References