

# Three Effective Methods for Passivation of Perovskite Solar Cell Defects

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## Abstract:

Perovskite solar cells have garnered significant attention due to their outstanding photoelectric properties. However, the majority of widely used perovskite polycrystalline ion crystal films are prepared through solution treatment processes, which often lead to the formation of high-density defects during the crystallization process. These defects within the device can be quite severe and are a major contributor to non-radiative recombination, limiting the enhancement of photovoltaic performance and stability of solar cell devices. In this paper, we review the latest advancements in defect passivation strategies for perovskite crystals, encompassing Lewis acid, Lewis base, and Lewis acid-base synergy approaches. We delve into the regulatory mechanisms and passivation effects of these various strategies on perovskite surface/interface defects. Furthermore, we anticipate the application of these defect passivation techniques in future studies, hoping to further enhance the performance and stability of perovskite solar cells.

**Keywords:** perovskite solar cell, passivation, defects, lewis acid, lewis base

## 1. Introduction

The energy crisis has long been a pivotal challenge for the progress of human society. Currently, China relies heavily on fossil fuels, but the combustion of these fuels results in significant CO<sub>2</sub> emissions and dwindling fossil energy reserves. Consequently, the need to identify novel and abundant energy sources is becoming increasingly urgent. Solar energy, boasting the virtues of cleanliness, environmental friendliness, pollution-free nature, and inexhaustibility, has emerged as one of the most promising energy sources for future development. Particularly noteworthy are perovskite solar cells (PSCs), the third generation of solar cells, which exhibit high efficiency even in low-light conditions, low manufacturing costs, and ease of preparation. These attributes have garnered widespread attention from researchers worldwide in recent years.

## 2. Perovskite Solar Cell

### 2.1 Crystalline structure of perovskite solar cell

The crystalline structure of a typical AM(II)X<sub>3</sub> halide perovskite is shown in Figure 1a, where the A site is a monovalent organic cation with a large radius, such as FA<sup>+</sup>, MA<sup>+</sup>, etc., and can also be an inorganic cation such as Cs<sup>+</sup>, Rb<sup>+</sup>, etc.; The M site is a divalent metal cation, usually Pb<sup>2+</sup>, Sn<sup>2+</sup>; The X position is the halogen anion such as: I<sup>-</sup>, Br<sup>-</sup>, Cl<sup>-</sup>, SCN<sup>-</sup> or their combinations. With the development of research, the M-position divalent cation can be replaced by a combination of monovalent cation and trivalent cation to form a double perovskite junction A<sub>2</sub>M(I)M(III)X<sub>6</sub>. Expanded three-dimensional double perovskite structures reveal a large number of potential novel halide perovskites (e.g., Cs<sub>2</sub>AgBiBr<sub>6</sub>, Cs<sub>2</sub>NaBiI<sub>6</sub>, Cs<sub>2</sub>AgInCl<sub>6</sub>), which opens up more possibilities for the development of next-generation photovoltaic materials (Fig. 1b) [2]. The

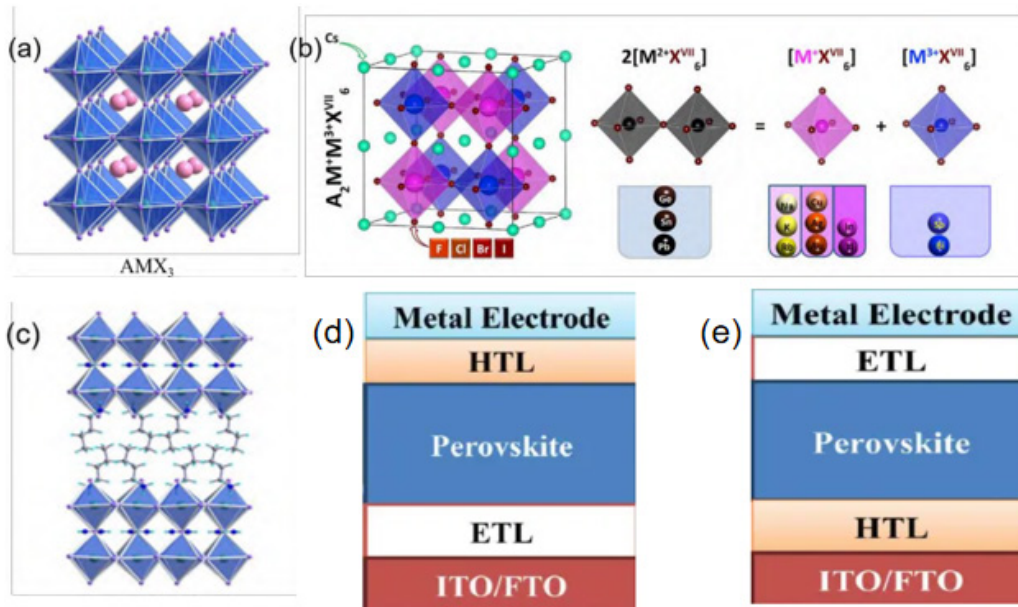
stability of the perovskite crystal structure can be calculated by the  $t$  and  $\mu$  ( $t$  is tolerance factor,  $\mu$  is octahedral factor):

$$t = \frac{R_A + R_X}{\sqrt{2}(R_X + R_M)} \quad (1)$$

$$\mu = R_M / R_X \quad (2)$$

Where  $R_A$ ,  $R_M$ ,  $R_X$ , represent the respective ionic radii of A, B, X, respectively. To make crystal stable at room temperature, a  $t$ -value of 0.9-1 is required[3]. In addition to the most widely studied three-dimensional(3D) halide perovskite, another common perovskite structure is the two-dimensional(2D) halide perovskite structure (Fig. 1c), which can be understood as the 3D structure is cut into sheets along the crystalline plane, halide ions are added to meet the surface metal coordination, and the larger cations enter the inorganic layer to form a two-dimensional structure [4].

As shown in Figure 1d, the device structure of PSCs includes transparent conductive oxide bottom electrodes (such as FTO and ITO), electron transport layer ETL (such as  $\text{TiO}_2$ ,  $\text{SnO}_2$ ,  $\text{ZnO}$ ,  $\text{C}_{60}$ , etc.), perovskite absorber layer (such as  $\text{MAPbI}_3$ ,  $\text{FAPbI}_3$ ,  $\text{CsPbI}_3$ , etc.), hole transport layer HTL (such as PTAA, Spiro-MeOTAD, P3HT,  $\text{CuSCN}$ , etc.), top electrodes (Au, Cu, Ag, carbon materials, etc.) [5]. PSCs can be divided into upright and inverted according to the position distribution of the carrier transport layer, and the device structure of the transparent conductive oxide bottom electrode/ETL/perovskite absorber layer/HTL/top electrode is generally called upright type (Fig. 1d). The device structure of the transparent conductive oxide bottom electrode/HTL/perovskite absorber/ETL/top electrode is referred to as an inverted type (Figure 1e). Although the carriers travel in different directions, they work on the same principle.



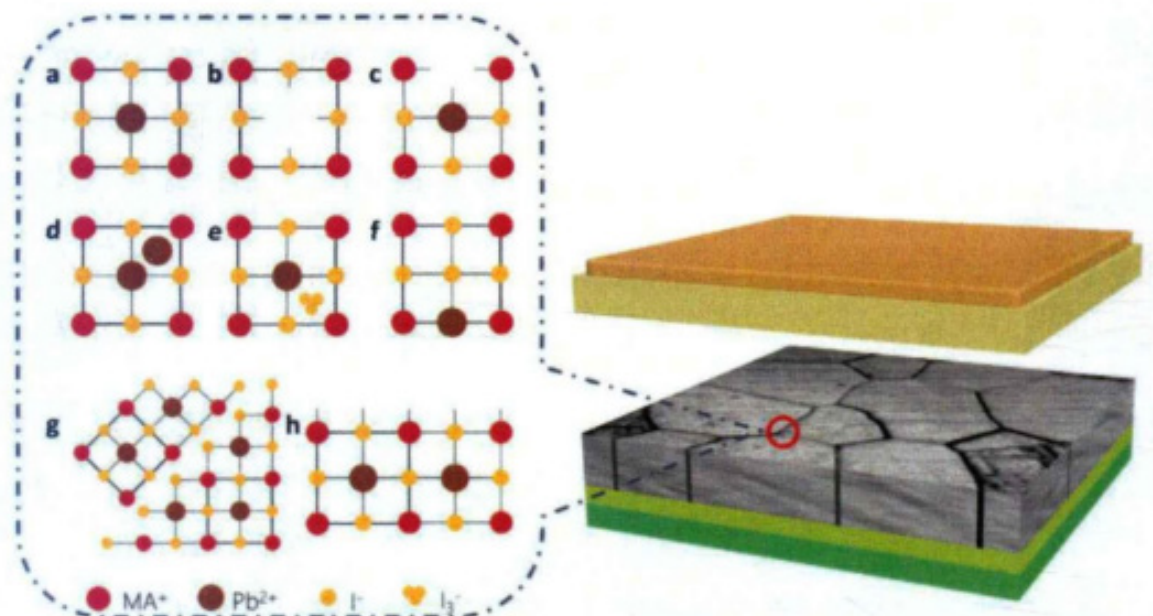
**Figure 1. (a) [4] Diagram of three-dimensional perovskite structure. (b) [2] Diagram of double perovskite structure, where  $\text{M}^{2+}$  ( $\text{Ge}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Pb}^{2+}$ , etc.) are displaced by a mixture of  $\text{M}^+$  ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ , etc.) and  $\text{M}^{3+}$  ( $\text{Sb}^{3+}$ ,  $\text{Bi}^{3+}$ , etc.). (c) [4] Diagram of two-dimensional perovskite structure. (d) Diagram of the structure of upright PSCs. (e) Diagram of inverted PSCs structure.**

## 2.2 Defects in perovskite solar cells

Perovskite thin film is a complex polycrystalline material, and the formation of dislocation is mainly due to the existence of grain boundaries. The zero-dimensional defects (point defects) in perovskite crystals and their formation mechanisms are shown in Figure 2, in which vacancy defects are formed by the detachment of some elements from the crystal surface during annealing, interstitial defects are formed due to impurities in the material entering the crystal lattice, and inverse defects are formed due to

the movement and replacement of ions. The surface of perovskite films prepared by solution method is mainly characterized by three types of point defects: inverse, vacancy, and gap [6,7]. Shallow level defects can be formed when the transition level is close to the valence band or conduction band and carriers trapped by shallow level traps have little effect on carrier recombination [8]. Deep level defects are formed when the transition levels are in the middle third of the band gap, which trap electrons or holes that cannot escape with the help of thermal activa-

tion and are annihilated by oppositely charged carriers by NRR, as described in the SRH theory [1].



**Figure 2. Schematic diagram of defect types in perovskite crystals: (a) ideal crystal structure, (b)  $\text{Pb}^{2+}$  vacancies, (c)  $\text{I}^-$  vacancies, (d) interstitial  $\text{Pb}^{2+}$ , (e) interstitial  $\text{I}^{3-}$ , (f) Pb-I substitution, (g) grain boundaries, (h) surface dangling bonds.**

### 3. Passivation of defects in perovskite

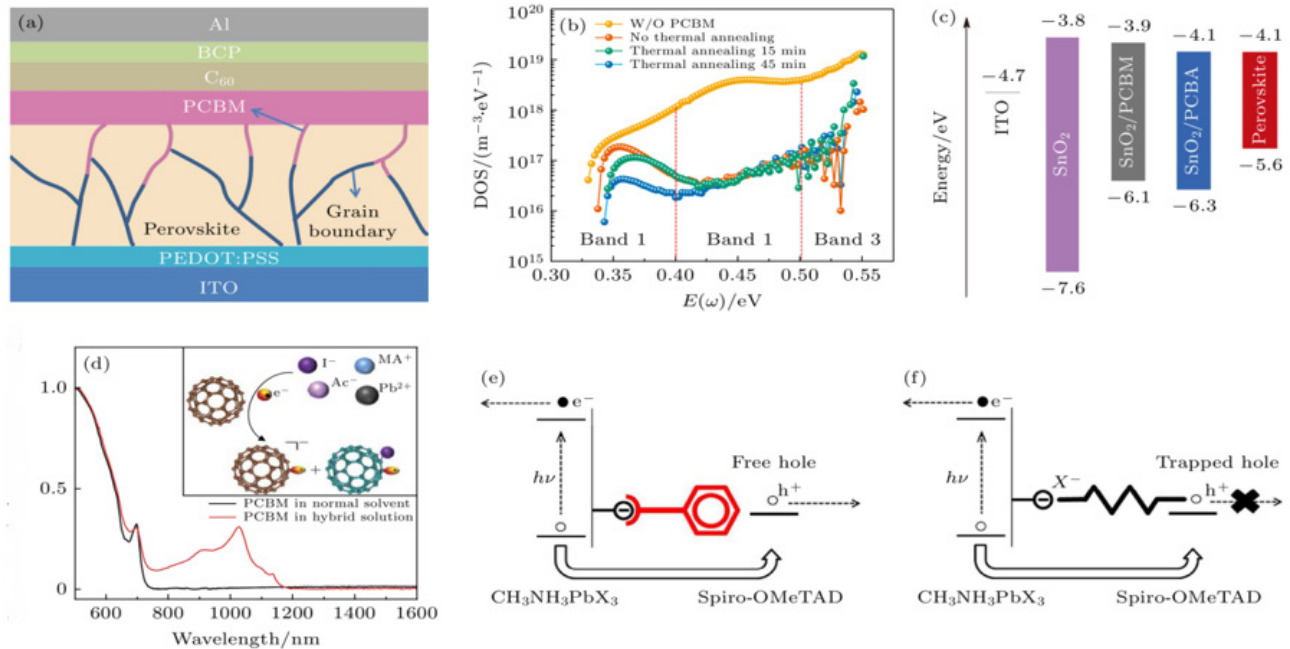
#### 3.1 Passivation of defects through Lewis acid

Currently, it has been found that fullerene ( $\text{C}_{60}$ ) and its derivatives (PCBM, PCBA, ICBA, etc.) can serve as Lewis acids to effectively passivate defects [10,11]. In the year of 2014, Shao's team [9] discovered that PCBM can passivate different defects at the interface between the particle boundaries of inverted PSCs and perovskite/ $\text{C}_{60}$ , as given in Figure 3a. PCBM can cut down surface charge recombination, reduce defect density, and greatly reduce photocurrent hysteresis (Figure 3b). The use of fullerene and its derivatives as electron transfer layers (ETLs) for surface passivation of  $\text{SnO}_2$  can improve the performance of devices. Wang's team [11] discovered the impact of  $\text{C}_{60}$  and its derivatives on the property of  $\text{SnO}_2$ /perovskite devices. The surface dipoles augment the work function of ETL for PCBM and PCBA (Figure 3c). The device performance and repeatability are greatly improved through PCBA passivation with  $\text{SnO}_2$ .

This work emphasizes that interface chemical reactions are significantly important in the preparation of efficient

and firm PSCs when designing interface molecules reasonably. Xu's team [12] premierly reported the effect between PCBM and PSCs, and absorption spectra showed that the effect between PCBM and I<sup>-</sup> in solution formed free radicals (Figure 3d). Density functional theory (DFT) calculations indicate that PCBMs on solid surfaces or boundaries of grain interact with defects which rich in halide, hybridize with the surface, passivate defects, and improve performance of optoelectricity.

In addition to fullerene and its derivatives, Abate et al. [13] demonstrated that iodine pentafluorobenzene can be used for interface modification of perovskite/Spiro MeOTAD by passivating low coordination halide ions through halide bonding. Iodine pentafluorobenzene, which has weak electronegativity, can be used for interface modification of perovskite/Spiro MeOTAD. The electron density on the benzene ring of fluorobenzene is significantly reduced. This is because the five fluorine atoms can take electrons away from the aromatic ring, ultimately form a structure called supramolecular halogen bond complexes between iodine pentafluorobenzene and low coordination halides or Pb-X anti defects, as shown in Figures 3e and f.



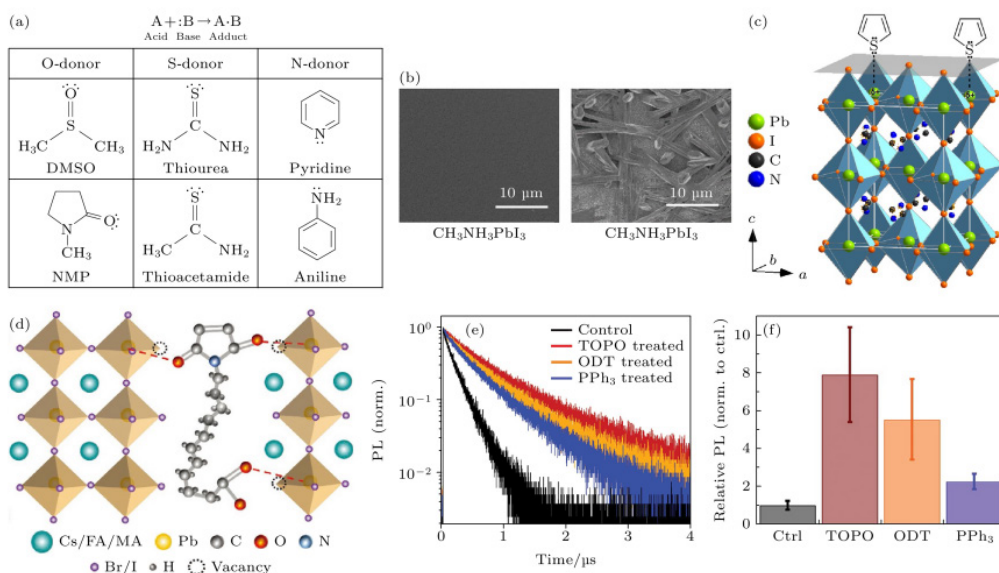
**Figure 3. (a) Structure of component with PCBM layer. (b) Diagram of trap density of states (tDOS). (c) Diagram of the energy bands of perovskite films and ETL substrates. (d) The absorption spectra of ultraviolet (UV)-visible of the hybrid solutions. (e) Diagram of the electrostatic screening of the halide ( $X^-$ ) on the perovskite surface. (f) Charge trapping between the undercoordinated halide and the hole.**

### 3.2 Passivation of defects through Lewis base

The unstable property of organic cations (such as  $FA^+$ ,  $MA^+$ ) and iodides during crystallization in the time of annealing can bring on the formation of low coordination  $Pb^{2+}$ . NRR can significantly influence low coordination  $Pb^{2+}$ , so it is necessary to passivate low coordination  $Pb^{2+}$  to increase device function. Based on Lewis acid-base chemistry, low coordination  $Pb^{2+}$  can be regarded as Lewis acid. Lewis base has a pair of electrons which non bonding to coordinate with low coordination  $Pb^{2+}$ , and form Lewis adducts. Figure 4a illustrates some examples of Lewis bases. Lee and his team [14] dissolved  $CH_3NH_3I$  and  $PbI_2$  in DMF and added equimolar amounts of DMSO to form an adduct of  $CH_3NH_3I \cdot PbI_2 \cdot DMSO$ , ultimately preparing a uniform  $MAPbI_3$  light absorption layer (Figure 4b). In contrast, precursor solutions without DMSO will form rod-shaped  $MAPbI_3$  crystals. This indicates that intermediate adducts contribute to the crystallization of perovskite and play a crucial role in controlling the crystal morphology. They can also reduce some defects and improve the photoelectric performance of PSCs. Noel and his team [15] first arranged to use Lewis base as donors of S or N to passivate the defects of low coordination  $Pb^{2+}$  (Figure 4c), significantly improving photovoltaic performance. Other functional groups which have lone electrons pair, like O

or P, also show Lewis base properties. Organic small molecules are widely used for passivating Lewis acid defects at interfaces due to their structural diversity. Zhu et al. [16] added 11 maleimide undecanoic acid (11MA) with carbonyl groups and long chains of hydrophobic alkyl to the precursor solution of perovskite. The study found that the use of 11MA can enhance the crystallization of perovskite, reduce the density of defect states, and extend the lifetime of charge carriers, resulting in a device efficiency of 23.34%, almost no hysteresis effect, and improved stability. The improvement in device performance can be attributed to the strong coordination between carboxyl and maleimide groups in 11MA molecules and  $Pb^{2+}$  to regulate crystal growth and passivate defects (Figure 4d). Secondly, hydrophobic long-chain alkyl chains can improve the water stability of perovskite films [16]. Using the same principle, deQuillettes et al. [17] deposited three Lewis bases (trioctylphosphine oxide (TOPO), 1-octadecanethiol (ODT), and triphenylphosphine ( $PPh_3$ )) onto  $MAPbI_3$  thin films through post-treatment. They found that after Lewis base optimization treatment, defects and NRR were reduced and PL was enhanced (Figure 4e, f), which could increase the PL lifespan by nearly an order of magnitude, reaching  $8.82 \pm 0.03 \mu s$ .





**Figure 4.**(a) Adduct formed from reaction between Lewis acid (A) and Lewis base (B). (b) SEM image of perovskite crystal with/without DMSO. (c) The excess positive charge neutralized by the thiophene molecule. (d) Passivation mechanism of 11 MA diagram. (e) Time-resolved photoluminescence decay diagram of films disposed with TOPO (red), ODT (orange), and PPh<sub>3</sub> (blue). (f) The samples and the films which used TOPO, ODT and PPh<sub>3</sub> diagram of integrated luminescence intensity.

### 3.3 Passivation of defects through Lewis acid-base synergy

At present, many methods of passivation can only passivate one type of the defects. It is an important criteria to preserve charge neutrality of passivating charged defects in perovskite films [18]. It is a tendency to use passivation molecules or kinds of additives which have dual functions of Lewis base and acid. According to that, Zhang's team [19] added N - (4-bromophenyl) thiourea (BrPh ThR) into a perovskite precursor solution and put Bis PCBM mixed isomers in an antisolvent, passivated Pb<sup>2+</sup> and PbX<sup>3-</sup> defects, and increased device efficiency up to 21.7%.

## 4. Conclusion and outlook

At present, the stability of PSCs is far from meeting commercial usage standards, which is closely related to various types of defects within the device structure. To improve device efficiency and stability and reduce hysteresis, it is necessary to effectively reduce NRR and conduct comprehensive defect passivation strategy research. This article summarizes the current main passivation strategies, mainly Lewis acid and Lewis base passivation on the surface and grain boundaries. In order to improve the passivation effect, the combination of multiple electron donors can maximize the Lewis acid-base passivation ability. It is of great significance to develop more effective and cost-effective Lewis acid passivators. In addition

to organic Lewis acids, researchers should also develop more stable inorganic Lewis acids to passivate negatively charged defects for achieving high efficiency and stability. Exploring the development of new pseudo halide anions is an important means of passivating cation defects (such as low coordination Pb<sup>2+</sup> and halide vacancies) in the future. Although passivation work gradually maturing, at present, the comprehending of passivation mechanism is of insufficiency, and the kind, concentration, and depth of traps generated by defects cannot be accurately identified. This may be because of the multifunctional properties and limited experimental techniques of some passivating agents.

In the future, efforts can be made to regulate the internal defects and device properties of devices from the following aspects: (1) Collaborative targeted passivation strategy [20]: Developing more efficient passivation agents and combining additives which complementary and multifunctional to produce synergistic effect of passivation. (2) Atomic scale analysis strategy [21]: It's crucial to accurately characterize and orientate defect types to defect control. (3) Crystal source control strategy [22]: In the way of optimizing the process of crystal preparation and composition, the formation of defects generated during the crystallization of perovskite films is restrained from the beginning.

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