Defect-states Passivation Strategy in Perovskite Solar Cells

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Abstract. In the modern era, energy demand rises dramatically accompanied by the rapid growth of our population, causing urgent energy shortages and environmental issues around the globe. People turned their attention to solar energy for an eco-friendly and economic solution, in which, perovskite solar cells emerged and had caught a great deal of attention in the past decades for their promising and commercial development potential. To fully release their capability for a high-performance device, defect mechanisms which are one of the main factors inhibiting the efficiency and stability, as well as passivation strategies must be thoroughly studied. In this review, the concept and formation mechanism of the defects are summarized, the corresponding defect characterization techniques regarding their working principles and downsides were also compared. Furthermore, substantial passivation strategies were discussed. Although perovskite solar cells still have a long way to go, facing difficulties in a lot of other aspects, we believe that the research we are doing now is of great significance in making perovskite into a real application.

1 INTRODUCTION

Perovskite solar cell is a kind of solar cell that employs hybrid organic-inorganic metal halide as core light-harvesting materials. It has occupied a leading position and become one of the hot spots in the photovoltaic research field owing to its economical manufacture costs, simple solution processing fabrication, and rapidly boosting photoelectric conversion efficiency (PCE), which has attracted great attention from the business market since its potential for next photovoltaic evolution. The PCE has skyrocketed from 3.8% [1] in 2009 to 25.5% [2] this year, with the help of strong light-harvesting ability [2], small exciton binding energy[3], fast charge transport properties[4], and prolonged charge carrier lifetime[5]. Perovskite is a special crystal structure with the chemical components simplified in ABX_3, generally, in our case, A is small organic molecules or metal cations (Cs^+, MA^+, FA^+), B refers to divalent metal cations (Pb^{2+}, Sn^{2+}, Ge^{2+}, Cu^{2+}) and X represents halide (I^-, Br^-, Cl^-). The classical perovskite photovoltaic material is $CH_3NH_3PbI_3$, in which the halogen ions are located in the octahedral top with the lead wrapped in the center of the octahedral cage, and the organic methyl amino groups located at the top angles of the face-centered cubic lattice.

From the lessons learned from dye-sensitized solar cells (DSSCs), the first perovskite device structure was mesoporous superstructure, in which a large number of mesoporous TiO_2 were adopted to support the perovskite materials, and also played a role in electron transport. [6] Further studies demonstrated the superior charge transport properties of perovskite itself and led to the birth of the planar structure. In a planar junction perovskite solar cell,

several hundred-nanometer thick absorber layers were sandwiched between the electron transport layer (ETL) and hole transport layer (HTL) without a mesoporous scaffold. Despite its shorter development period, it provided an efficiency of over 15% and provide simplified device configurations at that time.[7] Inverted perovskite has a device structure known as "p-i-n", in which HTL is at the bottom of intrinsic perovskite layer i with ETL n at the top, in which light was illuminated through the HTL surface. In recent years, a novel kind of multidimensional perovskite has become promising candidates to surmount several challenges in perovskite devices, especially, long-term stability. Mostly, it forms a ruddlesden–popper structure with the help of aliphatic or aromatic alkyl ammonium cation[8].
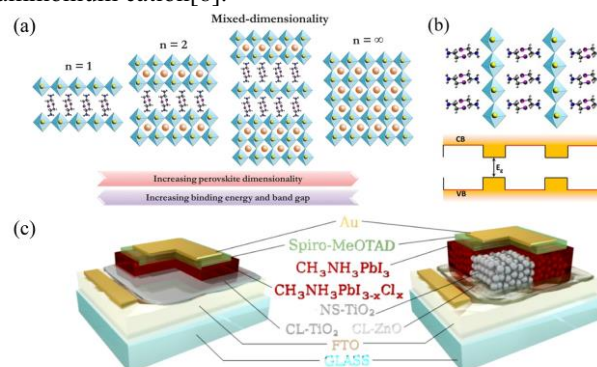

Fig.1. (a) The crystalline structure of multidimensional perovskites, including 2D perovskites (n=1 and 2, where n represents the metal halide lattices), mixed-dimensional perovskites, and 3D perovskites (n=1). Adapted from Ref. [9]. Copyright 2016 Wiley-VCH Verlag GmbH & Co.KGaA. (c) Typical perovskite solar cell device structure: (Left) planar

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structure, (Right) mesoporous scaffold. Adapted with permission from ref. (10). Copyright 2014 American Chemical Society

2 DEFECTS IN PEROVSKITE SOLAR SYSTEM

Despite the fast advance in the perovskite performance, the existence of defects leads to compromised PCE due to non-radiative recombination centers and trap induced charge injection barriers, which results in a gap between the current PCE and the theoretically deduced Shockley-Queisser limit.【11】 The defects or trap-states have negative impacts on both the electronic and optic properties. In laser and LEDs, deep-level defects encouraged non-radiative recombination and lower the photoluminescence quantum yield, the radiative recombination at shallow defects also broadened the emission spectrum. Nevertheless, defects significantly accelerate the efficiency drop under the outdoor environment and hinder the long-term stability issues. Therefore, studying, and depressing defects in perovskite is a vital topic for perovskite future practical applications.

The defects in semiconductors can be classified into several categories. Point defects are one of the most important ones, includes vacancies, interstitials, and antisites, which are caused by missing atoms, extra atoms, and exchanged atoms, respectively. Aside from point defects, there can be line (one-dimensional) defects, where lattice periodicity is discontinuous along a line. Defects can develop into even higher dimensions, such as two-dimensional surface defects and grain boundaries, and three-dimensional voids and precipitates. The defects can be described according to two criteria. One is the formation energy of defects, which determines the probability of a defect type to exist in the material. The smaller the formation energy, the easier the defect can be triggered and generated. Another criterion is the position of the defect energy levels compared to the valence band maximum (VBM) and conduction band minimum (CBM). For energy levels close to the VBM or CBM, they are referred to as shallow-level traps while those located in the middle third of the forbidden bandgap are referred to as deep-level traps. Shallow-level traps can release the trapped charge carriers back to the band edges especially at elevated temperatures [12,13] whereas the deep-level traps cannot detrap charges easily.
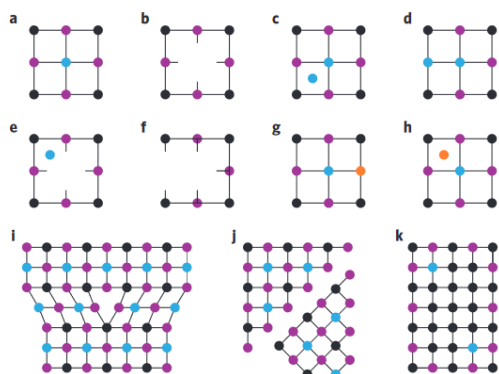

Fig. 2. Various kind of defects: a, perfect lattice; b, vacancy; c, interstitial; d, anti-site substitution; e, Frenkel defect (interstitial

and the vacancy created from the same ion); f, Schottky defect (anion and cation vacancies occurring together); g, substitutional impurity; h, interstitial impurity; i, edge dislocation (line defect propagating along the axis perpendicular to the page); j, grain boundary; and k, precipitate.

2.1 Passivation Strategies in Perovskite Solar Cells

For halide perovskites with un-passivated interfaces, large grain boundaries and high defect density would strongly enhance the activity of trap-assisted recombination channel, which is a major loss in halide perovskite-based photovoltaics.[14] Trap assisted recombination at interface defects is even more detrimental than grain boundaries, by solely passivating interface traps, the PCE can be enhanced by 40% [15]. When a defect state, lies energetically within the semiconductor bandgap, there is a likelihood that an approaching electron or hole will become captured or trapped. The trapped electron (or hole) is likely to be emitted, or de-trapped back to the conduction (or valence) band by phonon absorption if the activation energy is sufficiently small. However, if the activation energy is large, then it is more likely that the trapped carrier will annihilate or recombine with an opposite carrier before it can be emitted. Therefore, as a kind of polycrystalline thin film, perovskite thin-film must have a low density of charge carrier traps (16). Controlling charge carrier trapping is an extremely important issue in the development of high-performance solar cells.

Passivation, in physical chemistry and engineering, refers to a material becoming "passive", that is, less affected or corroded by the environment in which it will be used. Passivation involves the application of an outer layer of a shielding material as a micro-coating, created by chemical reaction with the base material [17]. The transition process from the "active state" to the "passive state" by the formation of a passivating film [18]. For perovskite solar cells, passivation generally refers to either chemical passivation, which reduces the defect trap states to optimize the charge transfer between various interfaces, or physical passivation, which isolates certain functional layers from the external environment to avoid degradation of the device.

2.1.1 Surface passivation by Lewis acid/bases

Surface passivation for organic-inorganic halide perovskite solar cells by introducing the Lewis bases thiophene and pyridine were proposed, curbing the formation of Pb defects and non-radiative recombination centers, which largely increases the PL quantum yield, PL lifetime as well as the PCE of the device. [19,20] The possible nature of the passivation mechanism is that the Lewis bases might donate electrons to bare Pb atoms originated from halide vacancy. Another Lewis base IT-M also helps to achieve an efficiency of 20.5% with a fill factor of 81%, since it stabilizes the Pb octahedrons in the ambient environment [21].

On the other hand, hole traps could be healed via Lewis acid. Iodopentafluorobenzene (IPFB) is a type of Lewis

acid that helps to coordinate halogen atoms[22,23] via supramolecular halogen bonding.(24,25) By immersing annealed halide perovskites in the IPFB and drying under N_2, the traps of halide perovskites can be effectively passivated, which prevents charge accumulation and recombination at the interface.

2.1.2 Grain boundary passivation

Fullerene derivatives are a kind of famous superstar materials used in an organic photovoltaic system, while in perovskite devices, they were usually used in inverted p-i-n structured perovskite solar cells. The fullerene layers deposit on the perovskite layers, eliminating photocurrent hysteresis and improving the device performance. [26] An ultra-thin PCBM layer was coated on the perovskite surface, followed by heat treatment, during which the PCBM diffused into the grain boundaries, where plenty of defects gathers. It passivates the PbI_3 anti-site defects during the formation of perovskite grains.[27]

In perovskite, self-passivation is a superior property that achieves perovskite. There are three methods to introduce a PbI_2 passivation layer at perovskite grain boundaries. The first one is the self-induced formation of PbI_2 from the controlled degradation of pristine perovskite thin films via thermal[28,29,30,31] or water vapor treatment [32-34]. The second is the preparation of a non-stochiometric perovskite precursor solution with an excess of PbI_2 (usually 3%-10% molar ratio relative to the perovskite[35-38]; and the final one is the incomplete reaction of PbI_2 through a two-step solution or vapor reaction method[37-39]

Another key component that constructs perovskite is CH_3NH_3I (MAI), which could also be introduced to complete self-passivation. This process was achieved by MAI vapor post-treatment, which was found to be an efficient method to passivate defect sites on perovskite grain surface[40,41].

2.1.3 Bulk Passivation via alky metal doping

In perovskite devices, the photocurrent hysteresis phenomenon is an inevitably involved issue that should be addressed. In recent years, a universal strategy named alky metal doping strategy is proposed. Time-resolved photoluminescence (TRPL) and Photoluminescence quantum efficiency (PLQE) measurements show that potassium doping is an efficient procedure to perform trap state passivation. The PCE of the passivated device would jump from 17.3% to 21.5%, accompanied by the enhancement of V_{OC} (Open-circuit voltage) and J_{SC} (Short-circuit current density). Besides, the ion migration is also inhibited in that observation, which strongly hindered the hysteresis.[49,50,51]

2.1.4 Passivation of the charge carrier transport pathways

Trap states located at the surface of the selected transportation layer are also crucial aspects. The typical ETL TiO_2 could be passivated by an ultrathin layer of TiO_2 (atomic layer deposition), or a chemical deposited $TiCl_4$ layer. [52]

Furthermore, lithium ions were adopted to facilitate the electronic properties of the TiO_2 mesoporous layer by reducing electronic trap states. Additionally, self-assembled fullerene derivatives, pyridine, and other semiconductor shell layers that possess high electron mobility could also be brought in to help the passivation of the TiO_2 layer. [53-55]

Aside from the functional materials involved in the operational devices, the selective electrodes could not be ignored to fulfill the performance enhancement procedures. An ultra-thin Ni surface layer could be applied to the Au electrode that functioned as both a physical passivation barrier and a hole-transfer catalyst [56], which would enhance photocurrent density and substantially better water stability [57,58]

2.1.5 Surface passivation for long-term stability

Long-term stability has always been a vital research topic from the very beginning when perovskite solar cells appear. Some organic materials that contain hydrophobic groups, such as polystyrene (PS) [42], poly(ethylene terephthalate) (PET), poly(methyl methacrylate) (PMMA) [43-45],Teflon [46,42], poly(4-vinyl pyridine) (PVP) [46,47], polyvinylidene-trifluoroethylene copolymer (PVDF-TrFE) [42], and even ionic liquids [48], could be brought to cover the surface. They have been used as protective polymer film on perovskite thin-film/arrays, and not only passivate surface defects but also block atmospheric moisture, allowing perovskite solar cells to sustain over 80% of their initial performance after 30 days of storage in high moisture (50%) condition[70].

2.2 Methods to evaluate the trap states properties

According to the abovementioned details about the trap-states in perovskite solar systems, it could be readily found that basic knowledge about the trap-states is vital in efficiency promotion strategy. Therefore, the priority is to capture the fruitful properties of the trap-states. Several classical techniques are summarized herein, accompanied by corresponding basic principles.

2.2.1 Space-Charge-Limited-Current (SCLC)

SCLC is a powerful method to estimate the density of defect states and charge mobility from measured current-voltage characteristics, it can be determined by the product of space-charge density derived from the permittivity of the semiconductor[59]

Defects can trap and scatter the free charge carriers, thus change the electrical properties of halide perovskites. Under charge injections through ohmic contacts, it can be found that there are three distinct regions in the log-log current-voltage curve. [60] When the voltage is relatively small, $I \propto V^n$ with n=1. This is the first region called the Ohmic region. The second region is the trap-filled limit (TFL) region, where the applied voltage reaches a certain threshold value V_{TFL}, the defects become saturated and are

not able to trap more free carriers. The resistance thus jumps to a lower value and n increases to above 3. The third region is called the Child region with n equals to 2 that follows the Mott-Gurney law[61]. The defects density can be derived with the assumption that all defects are filled, and injected charges can freely move,

$$n_{trap} = \frac{2\varepsilon\varepsilon_0 V_{\text{TFL}}}{qL^2} \qquad (1)$$

where n_{trap} is the defect density, ε is the relative dielectric constant to vacuum, ε_0 is the vacuum permittivity, q is the electric charge and L is the thickness[62].

Temperature-dependent SCLC can be used to defer the energy level of the defect relative to CBM and VBM,

$$\mathrm{E}trap = \frac{-d\ln(J)}{d(k_bT)^{-1}} \qquad (2)$$

with current density J, temperature T and Boltzmann constant k_B[63][64].

2.2.2 Density functional theory (DFT) calculation

The determined trap concentration via SCLC is not accurate as different charges cannot be differentiated, for instance, the potential of ion migration within the crystal resulting in underestimation of trap concentration. Knowing this situation, theoretical calculations, such as DFT methods, is necessary to explore the nature of traps because it is not possible to find out the origin of imperfections experimentally. DFT is a computational modeling method using supercells of a large number of atoms to investigate the electronic structure through functionals of spatially dependent electron density. The small formation energy of defect states in perovskite devices is estimated and the shallow distribution property is elucidated via DFT, which facilitates the strong trap states tolerance ability and prolongs the carrier lifetime in perovskite devices. (65）

2.2.3 Thermal admittance spectroscopy (TAS)

Defects could be deemed as an analog of small capacitors since the trapping-detrapping behavior can be considered as a charge-discharge process. By applying alternating current (AC), the admittance of the target halide perovskites will respond to the AC voltage. The relative position of the defect energy level to the Fermi level determines the probability the defects are occupied or not[66]. Temperature and frequency-dependent admittance could provide the density of trap states (tDOS) with a trap energy depth profile [67]by the following formula:

$$n_{trap,E} = -\frac{V_{bi}dC\omega}{qW_D d\omega k_B T} \qquad (3)$$

Where V_{bi} is the built-in heterojunction potential barrier, ω is the AC frequency, C is the capacitance and W_D is the depletion width of the space-charge region [68.69]. However, very deep traps or traps with long thermal emission time cannot be detected since this method depends on the dynamics of the trapping-detrapping process as well as the relative position of defect energy level and Fermi energy.

3 CONCLUSIONS

Perovskite cells have a promising potential in the future optoelectronic device market, although they are still facing instability and limited PCE undersides. To make it more competitive, we need a dedicated and comprehensive understanding of the defect behavior and mechanism in perovskite cell using various theoretical and experimental methods such as DFT, SCLC mentioned above, and from there we can devise the appropriate and effective ways for defect passivation, and rapid progress could be made in the field so far. Currently, we have so many different strategies for passivation using different materials on different parts, we have surface passivation using Lewis base/ acid, grain boundary passivation using fullerenes derivatives, bulk passivation through doping with alkyl metal, and even passivating charge carrier transport pathways. All these are crucial processes not only to increase the PCE, hinder hysteresis, and also improve long-term stability to make it a more resilient, durable, and competitive device in the future.

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