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Enhancing Open-Circuit Voltage and Fill Factor in Sn-Based Perovskite Solar Cells: Challenges and Opportunities for Sustainable Photovoltaics

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ABSTRACT

Tin (Sn)-based halide perovskite solar cells (PSCs) offer a promising lead-free alternative with favorable bandgaps and strong absorption, yet their performance is limited by substantial open-circuit voltage (V_{oc}) and fill factor (FF) losses. This review examines the primary origins of V_{loss} , mainly non-radiative recombination associated with undercoordinated Sn sites, deep-level defects, and the oxidation of Sn^{2+} , all of which elevate defect densities and accelerate recombination. FF degradation is further linked to Shockley–Read–Hall (SRH) trap-assisted recombination, reflected in increased ideality factors. The review also highlights advanced characterization approaches thermal admittance spectroscopy, drive-level capacitance profiling, and emerging machine-learning tools for probing carrier dynamics and quantifying non-radiative pathways. Although progress has been made, matching the V_{oc} and FF of Pb-based PSCs remains challenging due to the intertwined effects of oxidation chemistry, defect physics, and interfacial energetics. Recent strategies, such as molecular coordination, surface passivation, compositional engineering, and optimized charge-transport interlayers, show promise in suppressing recombination and improving energy alignment. Continued advances in defect passivation, oxidation control, and interface engineering are expected to be key to enabling efficient and environmentally sustainable Sn-based photovoltaic technologies.

1 | Introduction

The increasing global energy demand, driven by population expansion, urbanization, and industrial growth, has placed massive pressure on finite fossil fuel resources. The environmental consequences of nonrenewable energy sources, such as greenhouse gas emissions, air pollution, and climate change, have augmented the worldwide transition toward cleaner, sustainable choices. Among diverse renewable energy technologies, solar photovoltaics (PVs) stand out due to their extensive potential and environmental compatibility. Nevertheless, conventional silicon-based solar cells governing commercial platforms face limitations

due to high manufacturing budgets, energy-intensive fabrication processes, and limitations in flexible device applications.

In this framework, metal halide perovskite solar cells (PSCs) have rapidly appeared as a transformative class of PV materials over the past decade. Their extraordinary optoelectronic properties include a high absorption coefficient (10^5 cm^{-1}), long charge carrier diffusion length, low exciton binding energies (16–20 meV), and defect tolerance. Pb^{2+} cation plays an essential role in defining the electronic structure, predominantly through its $6s^2$ lone pair electrons that hybridize with halide p orbitals, resulting in a highly dispersive valence band (VB) and a direct

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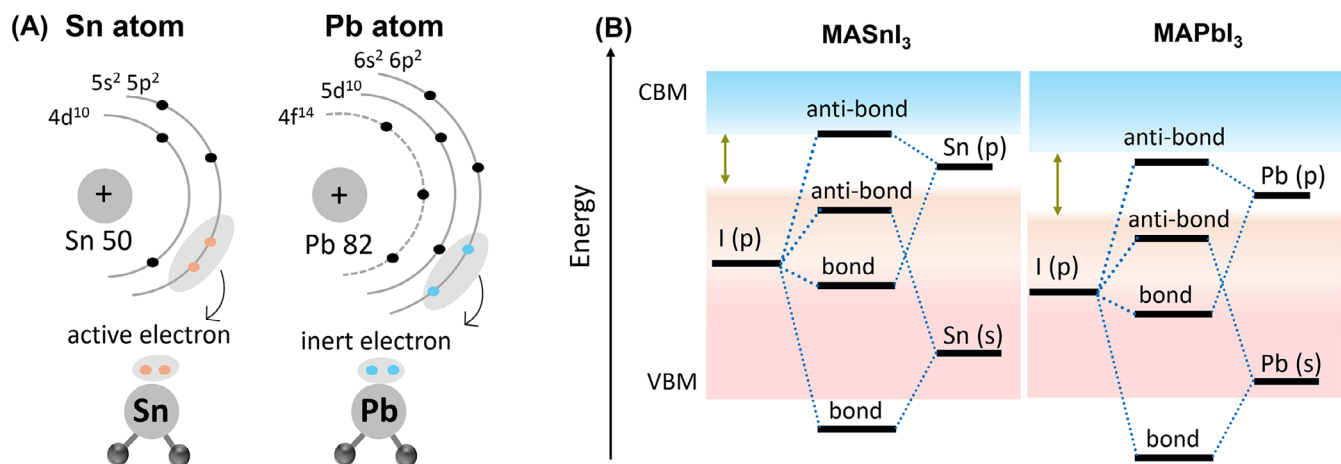


FIGURE 1 | (A) Comparison of the electronic structure of Sn and Pb atoms, depiction of active s electrons; (B) comparative schematic illustration of energy levels of MASnI₃ and MAPbI₃ perovskite.

bandgap (E_g) ideal for solar energy conversion. Regardless of achieving high power conversion efficiencies (PCEs) of over 26% [1], Pb-based PSCs face critical hurdles to scalability and environmental deployment. The high toxicity of Pb and its potential for leaching into the environment raise serious health and ecological concerns, driving the need for sustainable alternatives [2]. Besides, issues of intrinsic instability under exposure to moisture, oxygen, heat, and light further limit their long-term reliability and integration into commercial modules. These challenges have urged global efforts to identify less toxic B-site cations capable of replacing Pb²⁺ without compromising the material's optoelectronic properties.

Sn²⁺ stands out as the most structurally and electronically compatible alternative among the various Pb substitutes investigated. First, Sn²⁺ possesses a similar ionic radius (1.18 vs. 1.19 Å for Pb²⁺) and retains the s² electronic configuration, forming Sn halide perovskites with analogous lattice structures and favorable energy band alignments. Second, Sn perovskites possess direct narrow E_g (1.2–1.4 eV) compared to Pb-based perovskites (1.5–1.6 eV), enabling light absorption into the near-infrared region (NIR), high absorption coefficients, and superior intrinsic carrier mobilities relative to Pb-based systems [3, 4]. Their narrow bandgap (NBG) and high near-infrared absorption are ideal for bottom cells in all-perovskite tandem architectures. Third, Sn is abundant and less toxic, making it an environmentally friendly option. Despite these advantages, Sn halide PSCs face significant hurdles that impede their widespread adoption. The formation of defects and oxidation of Sn²⁺ to Sn⁴⁺ destabilize the perovskite structure, leading to performance degradation [5]. The primary cause of Sn oxidation is attributed to the absence of the lanthanide contraction (i.e., relativistic Lorentz contraction) in its outer electronic shells. In contrast, Pb exhibits the lanthanide contraction effect, wherein poor shielding by 4f electrons leads to the 6s electrons being drawn closer to the nucleus, resulting in a smaller atomic radius and rendering the 6s electrons more inert. Consequently, the 6s² lone pair in Pb remains less chemically active. However, in Sn, the lack of this relativistic contraction increases the availability of 5s electrons for reaction, imparting higher Lewis acidity to SnI₂ compared to PbI₂ (Figure 1A). In MASnI₃ (MA = methylammonium) perovskites, the Sn-5s

orbitals exhibit higher energy levels and steeper conduction band minimum (CBM) and VB maximum (VBM) edges compared to the Pb-6s orbitals in MAPbI₃ (Figure 1B). This results in weaker Sn–I bonding owing to the lower ionization potential of Sn. The reduced bond strength in Sn perovskites facilitates their rapid interaction with H₂O and O₂, promoting the formation of H–I and Sn–O bonds and consequently accelerating Sn²⁺ oxidation.

Recent developments in Sn halide PSC technology have achieved notable device efficiencies surpassing 15% [6, 7]. These high-performance devices demonstrate a V_{oc} of approximately 0.85 V and a fill factor (FF) near 73% for Sn halide perovskite absorbers with a bandgap close to 1.4 eV. Nevertheless, the theoretical limits for V_{oc} and FF in a single-junction solar cell with this bandgap are approximately 1.12 V and 89% [8], respectively, suggesting significant non-radiative recombination losses and charge transport inefficiencies. V_{oc} and FF are critical parameters that determine the PCE of PSCs, as they represent the maximum voltage output achievable under open-circuit conditions. It is directly related to the splitting of quasi-Fermi levels for electrons and holes and is fundamentally limited by the E_g of the absorber material [9]. Consequently, improving V_{oc} is essential for boosting the overall performance of PSCs. Ideally, V_{oc} approaches the thermodynamic limit of E_g/q , but in practice, various energy loss mechanisms cause significant deviations. In Sn halide PSCs, the V_{oc} is typically much lower than in their Pb-based counterparts, with reported values often exhibiting deficits greater than 0.5 V relative to the Shockley–Queisser (SQ) limit for the given E_g (~1.3–1.4 eV) [10]. These losses primarily originate from non-radiative recombination pathways facilitated by deep-level trap states (bulk Shockley–Read–Hall [SRH] recombinations), where the photo-generated electrons and holes recombine and dissipate energy as heat, high background carrier concentrations, and interfacial defects, all of which reduce the quasi-Fermi level splitting (QFLS) [11]. Furthermore, the spontaneous oxidation of Sn²⁺ to Sn⁴⁺ introduces trap-rich defect states and leads to heavy p-type self-doping, exacerbating non-radiative recombination and contributing significantly to V_{oc} loss (V_{loss}) and FF loss. The V_{loss} between the E_g and the actual V_{oc} can be described as $V_{loss} = E_g/q - V_{oc}$, and in high-quality solar cells, this value should be minimized to <0.4 V. However, in Sn halide PSCs, V_{loss} often

exceeds this threshold due to poor defect tolerance and unstable oxidation states. Therefore, understanding and mitigating these energy loss channels is essential for enhancing V_{oc} and FF, which will be discussed in the next sections in detail.

In this review, we provide a comprehensive and systematic analysis of the factors contributing to V_{oc} and FF loss in Sn halide PSCs, with a particular emphasis on defect formation and its underlying mechanisms. The review begins by elucidating the evolution of defects, tracing their formation back to the early stages of precursor solution chemistry and deep defects (SRH recombinations). We critically explore how these defects evolve and act as non-radiative recombination centers, directly affecting V_{oc} and FF of the device (Section 2). We highlight state-of-the-art characterization techniques, including thermal admittance spectroscopy (TAS), drive-level capacitance profiling (DLCP), and artificial intelligence (AI), which enable deeper insight into carrier dynamics and non-radiative pathways (Section 3). Furthermore, we detail recent strategies developed over the past 5 years to mitigate V_{oc} and FF loss in Section 4. Finally, Section 5 offers the author's perspective on future research directions, emphasizing the need for fundamental advances to unlock the full potential of lead-free Sn halide PSCs.

2 | Evolution of Defects and Challenges in Realizing High V_{oc} and FF in Sn Halide PSCs

V_{oc} and FF losses in PSCs arise from a series of physically interrelated mechanisms: (1) non-radiative recombination processes, including bulk SRH and interfacial recombinations, which diminish the internal QFLS and consequently limit the maximum attainable V_{oc} ; (2) a mismatch between QFLS and V_{oc} that induces internal voltage drops; (3) trap-assisted SRH recombination and elevated defect densities (N_t), which increase the diode ideality factor (n_{id}), thereby reducing the FF even at constant V_{oc} ; and (4) series and internal resistances present within transport layers, interfaces, and electrodes.

Several obstacles complicate the achievement of high V_{oc} in Sn halide PSCs. One of the fundamental challenges constraining the V_{oc} in Sn halide PSCs originates at the initial stage. At the precursor solution stage, Sn^{2+} instability and oxidative vulnerability significantly affect intermediate complex formation, leading to intrinsic defect generation before film deposition. Primarily, in $SnI_2 \cdot 3DMSO$ ($DMSO$ = dimethyl sulfoxide) precursor complexes, the mitigation of I^- facilitates a redox reaction that oxidizes Sn^{2+} to Sn^{4+} , forming SnI_4 (Figure 2A). This oxidation process not only depletes the active Sn^{2+} species but also introduces self-p-type doping through the formation of Sn vacancies (V_{Sn}), which act as acceptor states. This phenomenon results in a high hole density detrimental to PV performance. The coordination environment in Sn halide perovskite systems is highly labile and chemically reactive, especially in polar solvents, which can promote partial oxidation and complex disproportionation reactions. $DMSO$, a widely used coordinating solvent in perovskite precursor chemistry, exhibits redox activity under thermal conditions. Studies are directly evident that $DMSO$ acts as a chemical oxidant, transforming $Sn(II)$ into $Sn(IV)$ even under inert conditions [12, 13]. This irreversible redox reaction produces SnI_4 , SnO_2 impurity, and dimethyl sulfide (DMS) ($2(CH_3)_2S$) as byproducts (Figure 2B).

These disruptions in the coordination equilibrium facilitate the early incorporation of native point defects during crystallization. Second, during the film formation stage, the intrinsically high reactivity of Sn^{2+} , attributed to its strong Lewis acidity and chemically active $5s^2$ lone-pair electrons, induces rapid crystallization kinetics (Figure 1A). This accelerated nucleation and growth process often results in nonequilibrium crystallization, leading to poor film morphology, reduced grain size, and a high density of grain boundaries (GBs). Such disproportionate GB formation further facilitates the generation of intrinsic point defects, particularly V_{Sn} and halide vacancies (V_X), which serve as deep-level trap states (N_t) and non-radiative recombination centers, ultimately limiting the V_{oc} and FF of the device. As depicted in Figure 2C, various mechanisms continue to degrade the perovskite structure (Figure 2C), such as (i) halide ion migration, which induces dynamic defect formation near the surface and interface, compromising the V_{oc} and long-term operational stability of the perovskite. (ii) Uncoordinated Sn^{2+} and iodine-rich domains, arising from incomplete crystallization, enhance non-radiative recombination pathways and self-p-type doping issues. (iii) The situation is further aggravated by the oxidation of Sn^{2+} to Sn^{4+} , both during and after film formation. This oxidation introduces additional trap states, accelerates the degradation of the perovskite lattice, and destabilizes the optoelectronic properties. Moreover, oxygen from the environment can chemically interact with native defects, forming substitutional oxygen species that exhibit significantly enhanced non-radiative recombination rates. Similarly, halide vacancy defects are often incorporated at GBs and within the bulk and have been identified as potent non-radiative recombination centers that introduce deep-level trap states in the E_g , which will be further discussed in detail in the next section.

2.1 | Non-Radiative Recombination

This section explores the nature, origin, and impact of these intrinsic defects and their associated deep-level trap states and non-radiative recombination processes in Sn halide PSCs.

2.1.1 | Influence of SRH Traps, Trap States, and Ideality Factors on FF

Trap states significantly influence device performance by serving as SRH non-radiative recombination centers, which predominantly govern recombination processes in tin halide perovskites (Figure 3A). These trap states impede charge transport by inducing scattering from charged defect sites, consequently diminishing the material's conductivity. Furthermore, the FF can be quantitatively described as a function of the V_{oc} within the framework of the SQ model [14–16].

$$FF_0 = \frac{V_{oc} - \ln(V_{oc} + 0.72)}{V_{oc} + 1} \quad (1)$$

When SRH recombination dominates, both the recombination order and the voltage dependence of the recombination current are altered. Under conditions where deep mid-gap SRH recombination is dominant, the experimentally determined diode ideality factor approaches a value of approximately $n \sim 2$. An increase

Defects in solution

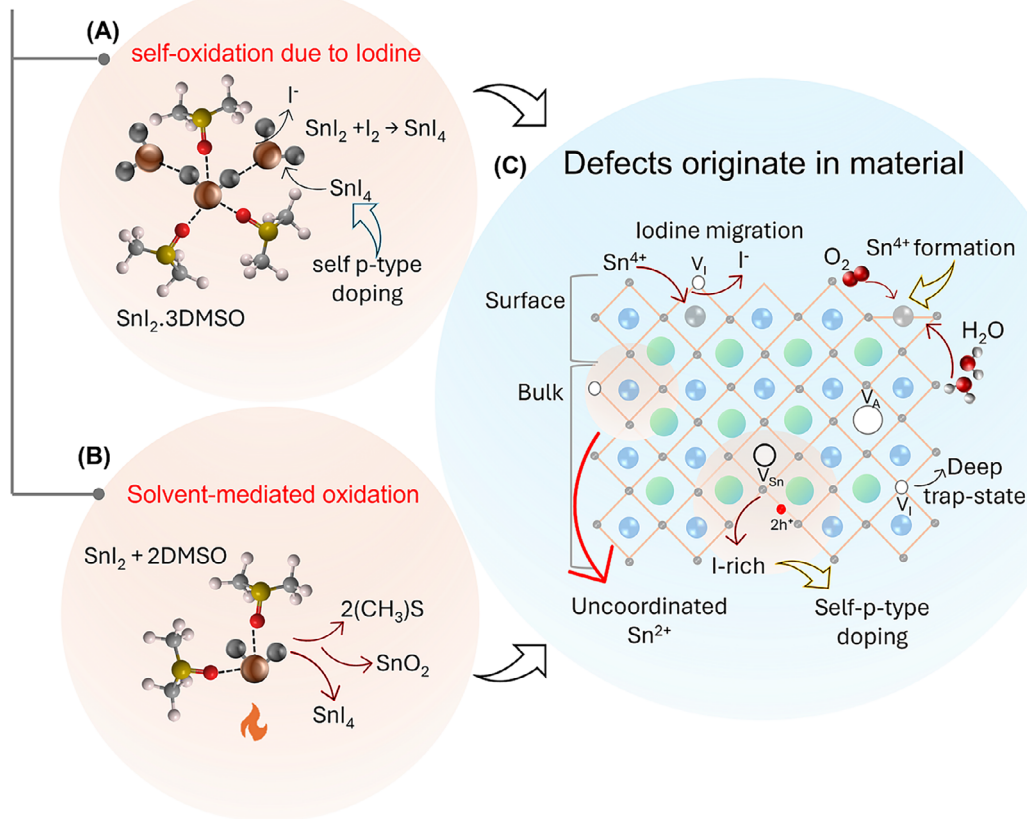


FIGURE 2 | Schematic illustration of the evolution of defects at various stages: (A) self-oxidation due to iodine; (B) solvent-induced oxidation at elevated temperature; (C) deep defect formation at the surface and bulk of Sn halide perovskite.

in the n_{id} leads to a reduction in the theoretical FF, even in the absence of resistive losses, as the FF at a given V_{oc} is influenced by the n_{id} via the normalized voltage,

$$V_{\text{oc}} = \frac{qV_{\text{oc}}}{n_{\text{id}}k_{\text{B}}T} \quad (2)$$

Iodine interstitials (I_i), A_{Sn} antisite defects (A site cation such as MA, FA), and iodine vacancies (V_I) are particularly damaging due to their low formation energies and their inclination to introduce trap density states within the E_{g} (Figure 3B,C) [17]. First-principles calculations reveal that the formation energy of V_I increases as the chemical potential shifts from iodine-poor to iodine-rich conditions in CsSnI_3 , the intrinsic Fermi level concurrently moves deeper into the VB. This shift partially offsets the increase in formation energy, allowing V_I to remain thermodynamically persistent. The V_I is expected to be present at substantial concentrations and serve as dominant non-radiative recombination centers in I-rich and I-poor conditions (Figure 3D) with carrier capture coefficients on the order of $10^{-8} \text{ cm}^3 \text{ s}^{-1}$. This high capture rate results in an SRH recombination coefficient of approximately $1.2 \times 10^8 \text{ s}^{-1}$ at typical defect densities (e.g., $3.5 \times 10^{15} \text{ cm}^{-3}$), corresponding to a carrier lifetime of just 8 ns, consistent with experimental observations of 3–7 ns under I-poor conditions [18]. Caprioglio et al. [19] demonstrated that SRH recombination occurring at the interface versus within the bulk material results in distinct n_{id} behaviors. Specifically, pronounced interfacial recombination can lead to an ideality factor approach-

ing 1; however, this scenario is associated with a reduced V_{oc} due to recombination taking place at a site that governs the terminal voltage. Conversely, bulk SRH recombination typically yields an n_{id} close to 2, as illustrated in Figure 3E [20].

2.1.2 | QFLS Mismatch Lowers V_{oc}

The V_{loss} in solar cells quantifies the energy loss that occurs during the photoconversion process and can be modeled using the balance theory. The V_{loss} [21] is defined as the difference between the material's E_{g} and the V_{oc} :

$$V_{\text{loss}} = \frac{E_{\text{g}}}{q} - V_{\text{oc}} \quad (3)$$

where E_{g} is the bandgap, and q is the elementary charge.

The V_{loss} in Sn-HP solar cells is predominantly governed by bulk non-radiative recombination mechanisms, including vacancy, interstitial, and antisite defect-induced trap states. These trap states arise from intrinsic deep-level defects and extrinsic impurities within the perovskite lattice, as well as from defect distributions at interfaces. Such defect-related energy states facilitate non-radiative SRH recombination pathways (see Figure 3A), which convert photogenerated charge carriers into thermal energy, thereby reducing the internal QFLS within the perovskite absorber.

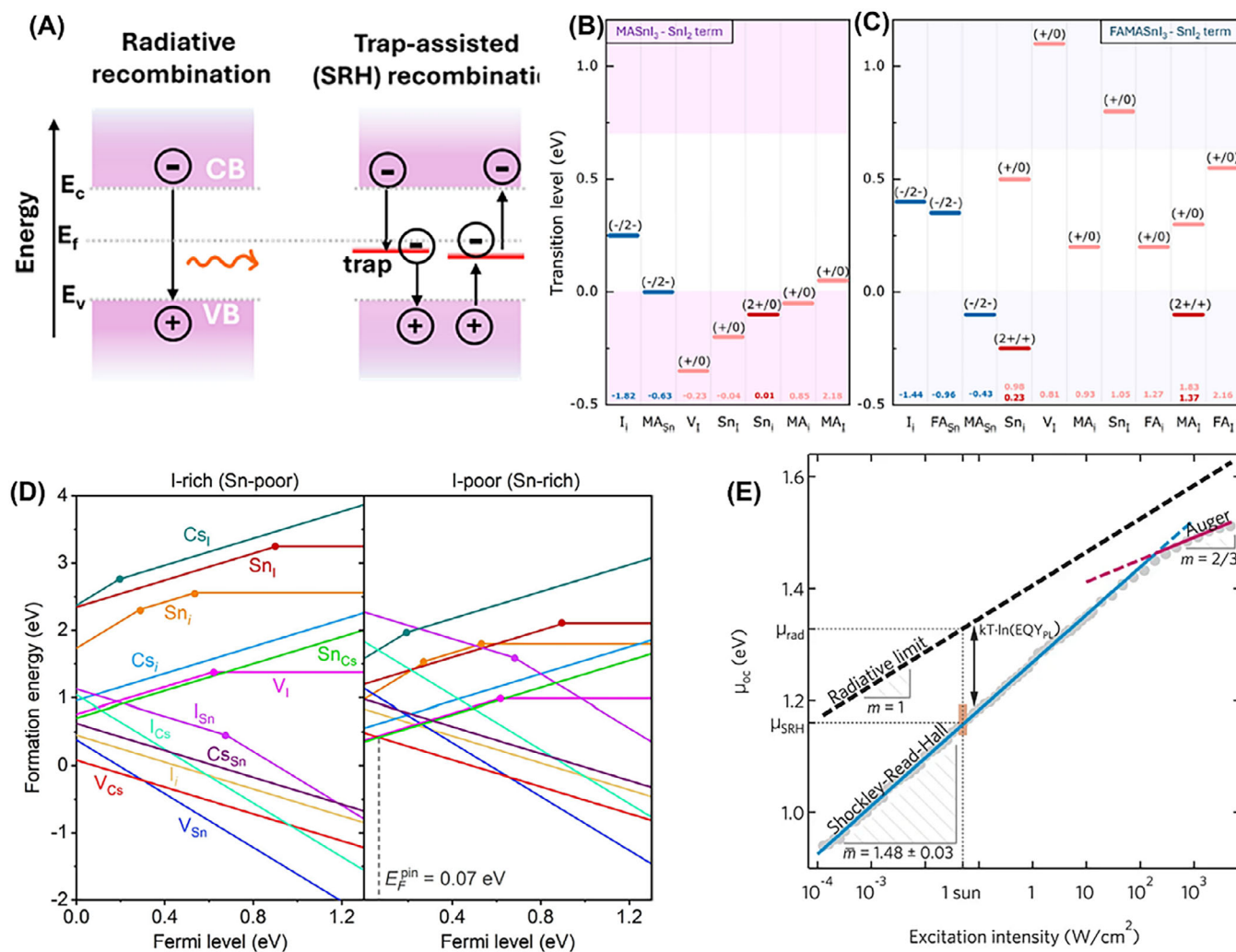


FIGURE 3 | (A) Schematic illustration of the recombination mechanism, which represents the direct radiative recombination and trap-assisted SRH recombination arising from deep defect levels. Formation energies of defects in various transition energy levels of (B) MASnI₃ and (C) FAMASnI₃. (D) Defect formation energies in CsSnI₃ under I-rich and I-poor conditions. (E) Free energy of the electron–hole pairs (μ) as a function of excitation intensity (I_{ex}), that is, μ - I_{ex} characteristics. CB, chlorobenzene; SRH, Shockley–Read–Hall; VB, valence band. *Source:* (A–C) Reproduced with permission [17]. Copyright 2024, American Chemical Society. (D) Reproduced with permission [18]. Copyright 2022, John Wiley and Sons. (E) Reproduced with permission [20]. Copyright 2017, CC BY 4.0 International License.

The QFLS quantifies the difference between the electron and hole quasi-Fermi levels under illumination and serves as an indicator of the maximum achievable photovoltage in the absence of non-radiative recombination losses. Ideally, the measured V_{oc} of a perovskite device corresponds to the internal QFLS divided by the elementary charge. However, in practical device architectures, a deviation occurs due to band bending of the quasi-Fermi levels near interfaces. This phenomenon primarily results from imperfect carrier selectivity of the charge transport layers (CTLs) or elevated surface recombination velocities at interfaces, causing the interfacial QFLS to be lower than the bulk QFLS (refer to Figure 4A). Consequently, interfacial recombination and asymmetries in charge transport induce a mismatch between QFLS and V_{oc} , manifesting as an apparent voltage loss even when the bulk perovskite material exhibits high radiative efficiency.

Simulations conducted by Warby et al. [22] demonstrate that factors such as low-mobility interlayers, energetic band mis-

alignment, mobile ionic species, and pronounced interfacial recombination contribute significantly to large QFLS- V_{oc} mismatches, thereby exacerbating apparent V_{loss} . The presence of low-mobility interlayers, misaligned band offsets, or limited conductivity in transport layers can induce photo-shunting effects and substantial FF reductions. Additionally, series resistance (R_s) indirectly intensifies recombination by impeding charge extraction, which leads to carrier accumulation near interfaces, increased SRH recombination rates, elevated n_{id} , and further degradation of both FF and V_{oc} . Therefore, voltage losses arising from non-radiative recombination and those due to QFLS- V_{oc} mismatches collectively contribute to reductions in the FF [23, 24].

The kinetics of non-radiative recombination in Sn halide PSCs can be modeled using a trap-assisted framework, where the recombination rate depends on both trap density and carrier capture efficiency. Studies on Sn halide perovskite indicate that

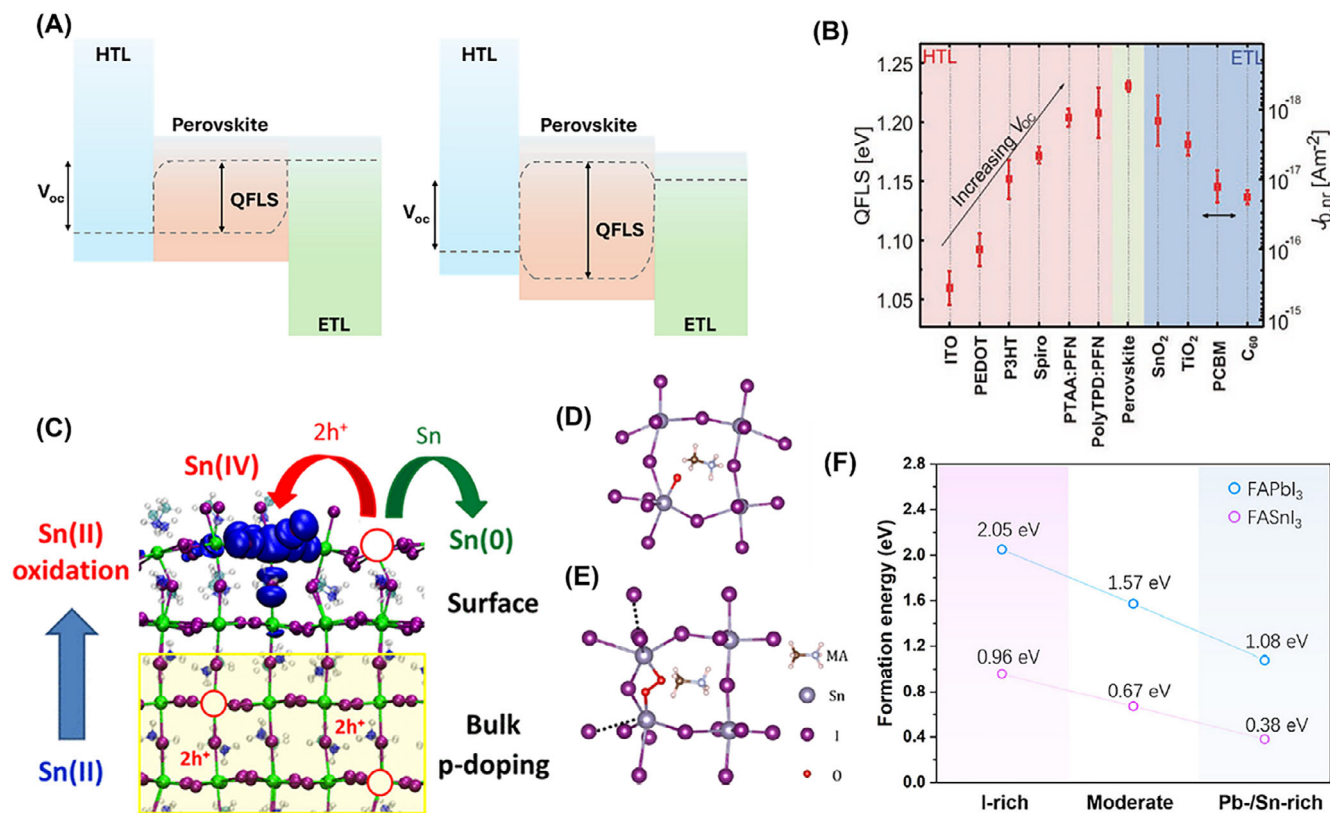


FIGURE 4 | (A) Schematic illustration representing an ideal and practical perovskite solar cell using hole and electron transport layers, representing the relation QFLS- V_{oc} mismatches. (B) QFLS was calculated from the photoluminescence of perovskite without the hole and electron transport layers. (C) Schematic illustration depicting the origin of self-induced p-type doping and Sn^{2+} oxidation in Sn halide perovskites. (D) The atomic structure of atomic oxygen (O_1^{2-}) and (E) molecular oxygen (O_2^{2-}) in MASnI_3 perovskite. (F) Defect formation energies of V_I in FAPbI_3 and FASnI_3 under I-rich, moderate, and I-poor conditions. ETL, electron transport layer; HTL, hole transport layer; QFLS, quasi-Fermi level splitting. Source: (A and B) Reproduced with permission [25]. Copyright 2021, John Wiley and Sons. (C) Reproduced with permission [26]. Copyright 2020, American Chemical Society. (D and E) Reproduced with permission [27]. Copyright 2023, American Chemical Society. (F) Reproduced with permission [28]. Copyright 2022, Royal Society of Chemistry.

the effective carrier lifetime (τ_{eff}) is governed by the interplay between radiative (τ_{rad}) and non-radiative ($\tau_{\text{non-rad}}$) components. For FASnI_3 ($\text{FA} = \text{NH}_2\text{CHNH}_2$), a common Sn halide perovskite composition, τ_{eff} is reported at 25 ns, whereas τ_{rad} is 277 ns, demonstrating that non-radiative recombination dominates the carrier dynamics [25]. A key challenge in these materials is the chemical instability of Sn^{2+} , which readily oxidizes to Sn^{4+} , particularly in the presence of oxygen. The formation of Sn^{4+} not only accelerates the degradation of the perovskite structure but also increases free hole density, thereby exacerbating non-radiative recombination through the introduction of deep trap states. To alleviate these losses and improve PV performance, it is imperative to improve the radiative quantum efficiency, which directly correlates with reduced non-radiative pathways and improved V_{oc} [25].

Unlike Pb-based perovskites, which exhibit a high tolerance to defects due to their shallow-level nature, Sn halide perovskites suffer from a higher propensity for intrinsic defects with deeper energy levels within the E_g , significantly undermining carrier lifetimes and QFLS [17].

The interfaces between the perovskite layer and CTLs also amplify non-radiative recombination in Sn halide PSCs. Poor

energy level alignment and interfacial defects introduce additional recombination channels that are readily occupied by charge carriers, thereby contributing to V_{loss} (Figure 4A). For example, the photoluminescence (PL) measurements of perovskite/CTL interfaces reveal a significant drop in QFLS when Sn halide perovskites are interfaced with common CTLs like poly(3,4-ethylenedioxythiophene) (PEDOT:PSS) or C_{60} , with QFLS values (Figure 4B) [25]. This reduction indicates that interfacial recombination currents exceed bulk losses in many cases, a challenge compounded by the p-type nature of tin halide perovskites, which exhibit high hole densities (10^{15} to 10^{17} cm^{-3}) due to self-doping. These excess holes occupy trap states near the VBM, enhancing non-radiative recombination [25].

2.2 | Self-p-Type Doping

The oxidation behavior of Sn in MASnI_3 exhibits a strong dependence on the local chemical environment. Density functional theory (DFT) calculations reveal that the conversion of Sn(II) to Sn(IV) is thermodynamically unfavorable in the bulk lattice but becomes energetically favorable at unpassivated perovskite surfaces. This contrasting behavior leads to the spontaneous reduction of bulk Sn(IV) to Sn(II) , accompanied by the release of

two holes into the VB, which induces intrinsic self-p-type doping and adversely affects the electronic properties (Figure 4C). In contrast, surface-stabilized Sn(IV) species act as deep-level electron traps, significantly enhancing non-radiative recombination pathways [26]. Studies suggest that the intrinsically low ionization potential of MASnI₃ accounts for alleviating tin vacancies and iodine defects, collectively aiding the characteristic self-p-type doping in Sn halide perovskites. V_{Sn} constructs an iodine-rich environment that can facilitate the oxidation of Sn(II) to Sn(IV). Furthermore, the elevated band edge energies of MASnI₃ lead to the formation of deep electron traps associated with undercoordinated Sn defects. Consequently, the defect chemistry in Sn halide perovskites is primarily influenced by Sn-centered defects [29]. Another study suggests that in CsSnI₃ perovskites, intrinsic p-type conductivity is predominantly attributed to the formation of cesium vacancies (V_{Cs}). The addition of excess Sn²⁺ can efficiently alleviate this behavior, as the chemical potentials of Sn and Cs are interdependent. Under such conditions, suppression of V_{Sn} formation inherently reduces the likelihood of V_{Cs} generation, thereby declining the concentration of acceptor-like defects and limiting hole accumulation [18].

2.3 | Oxidation-Induced Performance Degradation

Sn halide PSCs have emerged as less toxic alternatives to Pb-based counterparts, with strong potential for tandem PVs. However, their practical deployment is hindered by the facile oxidation of Sn²⁺, which significantly degrades device performance, particularly the V_{oc} . This sub-section elucidates the mechanisms driving oxidation-induced degradation and examines its impact on V_{oc} . Drawing on recent studies, it provides a comprehensive understanding suitable for a scholarly audience. The instability of the Sn²⁺ cation underpins the oxidation challenges in Sn halide PSCs, as it readily oxidizes to Sn⁴⁺ in the presence of ambient oxygen. This process is not a simple surface reaction but involves complex interactions with the perovskite lattice, particularly at defect sites. Two predominant mechanisms have been identified: oxygen-induced defect formation and superoxide-mediated degradation. In the former, oxygen interacts with native V_{I} within perovskites such as MASnI₃ (where MA denotes CH₃NH₃⁺). Rather than acting as a recombination center independently, oxygen binds to V_{I} to form substitutional oxygen defects. First-principles calculations demonstrate that the atomic oxygen (O_{i}) captures excess electrons, forming O_{i}^{2-} adjacent to a host Sn cation (Figure 4D). This induces a displacement of Sn toward the oxygen and repulsion of neighboring I atoms, leading to lattice distortion. Apart from isolated O_{i}^{2-} species, interstitial oxygen can strongly interact with native V_{I} , forming energetically favorable substitutional defects, where oxygen replaces an iodine site (O_{I}^{-}) (Figure 4E), amplifying non-radiative recombination rates. This deep-level trap accelerates carrier recombination, significantly reducing carrier lifetimes [27]. The second mechanism emerges under the combined effect of light and oxygen exposure (light/ O_2), where superoxide (O_2^{-}) plays a destructive role. In perovskites like FASnI₃, photoexcited electrons reduce O_2 to O_2^{-} , which subsequently reacts with the perovskite lattice, deprotonating organic cations and cleaving Sn–I bonds. This degradation yields products such as SnO₂, I₂, and organic byproducts, effectively decomposing the material. Studies have reported a significantly higher superoxide yield in FASnI₃ compared to

FAPbI₃, highlighting the greater vulnerability of Sn halide systems to photoinduced degradation under light and O₂ exposure. On the basis of the calculated chemical potentials of FA, I, and Pb/Sn within the stability regions (Figure 4F), the formation energies of V_{I} were evaluated for FAPbI₃ and FASnI₃ under I- to metal-rich conditions. In FASnI₃, the energy required to form V_{I} ranges from 0.38 to 0.96 eV (Sn- to I-rich), whereas in FAPbI₃, it increases significantly to 1.08–2.05 eV (Pb- to I-rich). These results indicate a substantially higher propensity for V_{I} formation in FASnI₃, facilitating more active sites for O₂ adsorption and subsequent superoxide formation [28]. These oxidation processes directly impair V_{oc} by amplifying non-radiative recombination and disrupting electronic properties. The introduction of O_{i} and superoxide generates deep-level trap states within the E_{g} , acting as recombination centers that capture charge carriers and diminish their lifetimes. For example, in MASnI₃, the SRH recombination rate constant surges from $9.3 \times 10^6 \text{ s}^{-1}$ (attributed to V_{I}) to $1.8 \times 10^9 \text{ s}^{-1}$ upon oxygen exposure, reducing carrier lifetimes by 2–3 orders of magnitude [27]. This escalation lowers the QFLS, a key determinant of V_{oc} . Additionally, oxidation products such as SnO₂ and secondary phases (e.g., FA₂SnI₆, SnI₄) alter the surface electronic structure [28]. Such changes misalign energy levels at interfaces with CTLs, hindering efficient charge extraction and further exacerbating V_{oc} deficits.

3 | Advanced Characterization Techniques for V_{oc} Analysis

Understanding the factors limiting V_{oc} in Sn halide PSCs requires advanced characterization techniques that probe carrier dynamics, surface properties, and recombination kinetics at various scales. These methods provide critical insights into the origins of V_{oc} deficits (Section 2). This section delves into advanced experimental methodologies, PL/time-resolved PL (TRPL), electroluminescence (EL), Kelvin probe force microscopy (KPFM), and impedance spectroscopy (IS), TAS, and DLCP, emphasizing their utility in elucidating V_{oc} -related phenomena in Sn halide PSCs. It also presents theoretical perspectives on V_{oc} analysis, encompassing machine learning (ML)-assisted modeling techniques and DFT simulations.

3.1 | PL/TRPL/EL Spectroscopy and Carrier Dynamics

PL and TRPL are essential, noninvasive analytical methods extensively utilized to investigate charge carrier dynamics in PSCs. These techniques provide vital insights into recombination mechanisms that directly affect the V_{oc} and FF. In Sn halide PSCs, losses in V_{oc} and FF are frequently intensified by non-radiative recombination and defect states. This section examines the application of PL/TRPL and EL measurements in elucidating carrier transport phenomena within Sn halide PSCs, drawing upon recent progress reported in the literature.

Baranwal et al. [30] employed PL and TRPL to verify that the incorporation of a phenyl-C₆₁-butyric acid methyl ester (PCBM) n-type dopant into Sn halide perovskites enhances electron extraction and mitigates interfacial recombination in Sn halide

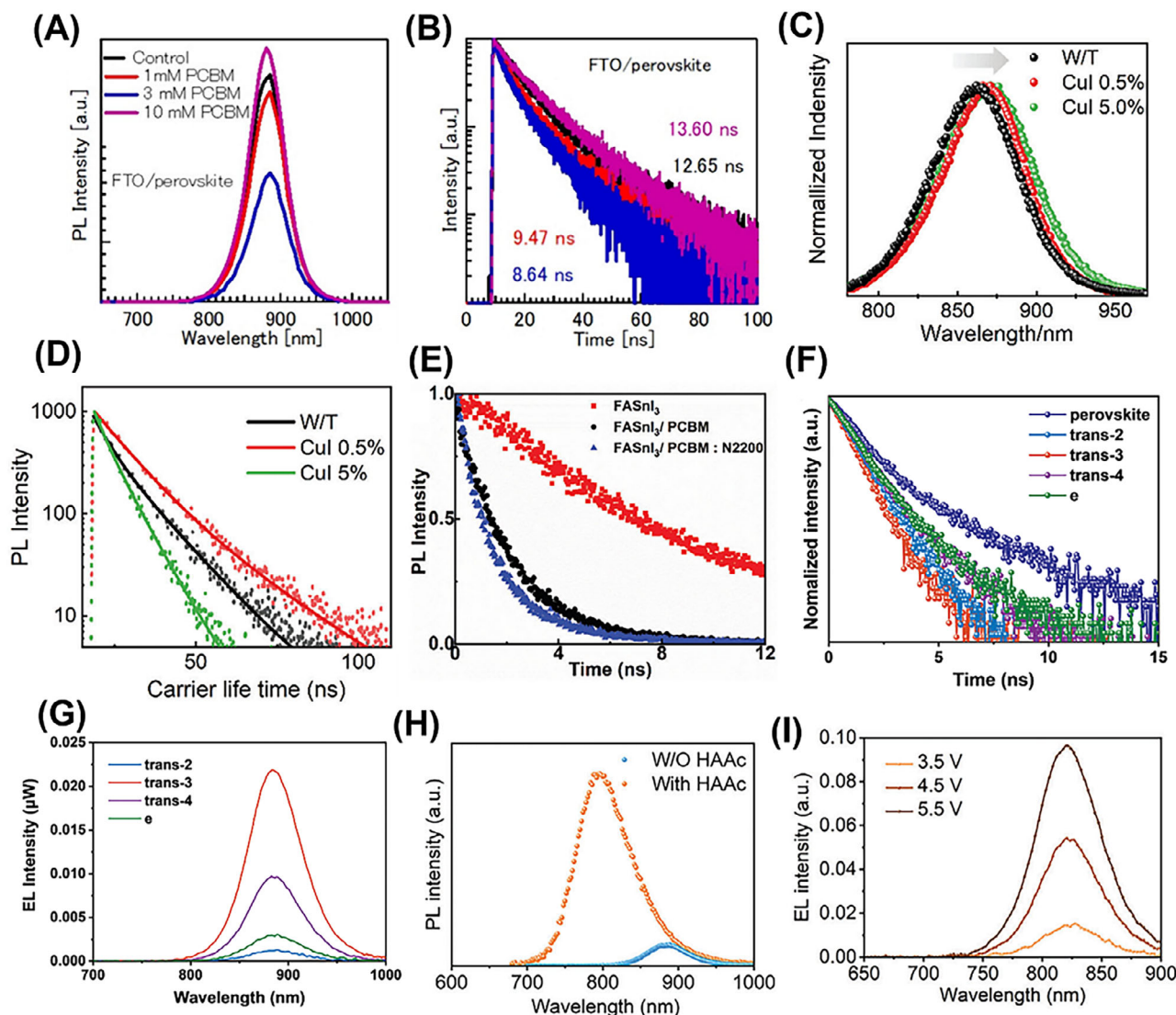


FIGURE 5 | (A and B) PL and TRPL spectra of the control film and PCBM-THP heterojunction perovskite films. (C and D) PL and TRPL spectra measured for Sn perovskite films without and with 0.5% and 5.0% CuI doping. (E) PL lifetime spectra of FASnI₃-, FASnI₃/PCBM-, and FASnI₃/PCBM-/N2200-coated perovskite films. (F and G) PL lifetime characteristic curves and EL spectra of perovskite and perovskite coated with *trans*-2, *trans*-3, and *trans*-4 transport layers under 2 V bias voltage. (H and I) Steady-state PL and EL spectra of perovskite LED without and with HAAC molecule. EL, electroluminescence; PL, photoluminescence. *Source*: (A and B) Reproduced with permission [30]. Copyright 2024, American Chemical Society. (C and D) Reproduced with permission [31]. Copyright 2023, John Wiley and Sons. (E) Reproduced with permission [32]. Copyright 2024, John Wiley and Sons. (F and G) Reproduced with permission [36]. Copyright 2023, John Wiley and Sons. (H and I) Reproduced with permission [37]. Copyright 2025, John Wiley and Sons.

PSCs. The PL spectra demonstrated significant quenching of emission intensity following PCBM addition, indicating efficient transfer of photogenerated electrons from the perovskite absorber to the electron transport layer (ETL), thereby reducing radiative recombination. Correspondingly, TRPL decay analyses revealed a marked decrease in carrier lifetime from 12.65 ns in the control perovskite to 8.64 ns in the 3 mM PCBM-doped perovskite, corroborating accelerated charge extraction and diminished carrier accumulation at the interface (Figure 5A,B). Furthermore, doping with CuI in Sn halide perovskites induced a red shift in the absorption edge, indicative of lattice contraction. The PL spectrum exhibited a red shift upon CuI doping, whereas TRPL measurements showed an increased carrier lifetime of 14.44 ns for 0.5% CuI-doped Sn perovskite compared to 10.75 ns in the control

film (Figure 5C,D). This enhancement suggests suppressed trap-assisted recombination, contributing to a high PCE of 10.5% ($V_{oc} \sim 0.63$ V) in hole transport layer (HTL)-free devices [31]. Significant PL quenching accompanied by a shortened lifetime of 1.9 ns was observed for FASnI₃/PCBM:N2200 films relative to FASnI₃ and FASnI₃/PCBM films (2.4 ns), indicating more rapid charge carrier extraction at the interface from Sn perovskite to PCBM:N2200 (Figure 5E). This improvement in charge extraction corresponded with enhanced device performance, achieving an efficiency of 12.98% [32]. Similarly, the incorporation of CsSnI₃ quantum dots onto three-dimensional (3D) perovskite films resulted in pronounced PL quenching and accelerated decay lifetimes, reflecting more efficient hole extraction at the perovskite interface [33].

In Sn halide PSCs, carrier lifetimes derived from TRPL are influenced by both radiative and non-radiative recombination pathways. For instance, Abudulimu et al. [34] utilized TRPL alongside transient photovoltage (TPV) and transient photocurrent (TPC) measurements to study carrier dynamics in high-performance Sn–Pb PSCs with a composition of $\text{Cs}_{0.05}\text{FA}_{0.7}\text{MA}_{0.25}\text{Pb}_{0.5}\text{Sn}_{0.5}\text{I}_3$. Their findings revealed that at low excitation fluences (1.1×10^{11} photons cm^{-2} pulse $^{-1}$), defect-assisted recombination dominates, yielding a carrier lifetime of approximately 3 μs , whereas at higher fluences, radiative recombination becomes significant (2×10^{-10} $\text{cm}^3 \text{s}^{-1}$), reducing the effective lifetime to $\sim 1 \mu\text{s}$ under 1 sun illumination. This dual-regime behavior underscores the sensitivity of TRPL to operational conditions and highlights its utility in dissecting recombination mechanisms that limit V_{oc} .

The ability of TRPL to correlate carrier lifetimes with V_{oc} is further exemplified by its integration with other techniques. TRPL-derived lifetimes were validated against TPV data in the same study, showing consistency between the trap-assisted lifetime ($\tau_{\text{nr}} \approx 3 \mu\text{s}$) and radiative recombination coefficient ($k \approx 1.9 \times 10^{-10}$ $\text{cm}^3 \text{s}^{-1}$) extracted from both methods. This agreement emphasizes that rigorous experimental control, such as varying bias light intensities, can refine lifetime estimates, enabling a clearer link between recombination dynamics and steady-state V_{oc} values (e.g., 0.874 V for their device). Such insights are crucial for identifying strategies to suppress non-radiative losses, primarily contributing to V_{oc} deficits in Sn halide systems.

Comparatively, Singh and Kabra explored recombination dynamics in pure Sn ($\text{MA}_{0.20}\text{FA}_{0.75}\text{Cs}_{0.05}\text{SnI}_3$), Pb–Sn-mixed ($(\text{MAPbI}_3)_{0.4}(\text{FASnI}_3)_{0.6}$), and pure Pb ($\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$) PSCs using TPV and TPC, though TRPL was not explicitly detailed [35]. Their work indirectly informs TRPL applications by demonstrating that pure Sn halide PSCs exhibit longer perturbed carrier lifetimes despite lower V_{oc} (compared to Pb-based counterparts), attributed to shallow defect states induced by Cs incorporation. Although TRPL was not the focus, the observed slow carrier relaxation aligns with trends reported in Sn halide perovskites via TRPL, where lifetimes can extend to microseconds due to defect-mediated processes [34]. Integrating TRPL into such studies could further quantify these lifetimes, offering a direct measure of how defect engineering impacts recombination and V_{oc} .

The versatility of TRPL extends to evaluating device stability, a critical factor in Sn halide PSCs prone to oxidation-induced degradation. Abudulimu et al. noted that unencapsulated Sn–Pb devices showed increased TPV lifetimes after light soaking, misleadingly suggesting improved carrier dynamics; however, concurrent V_{oc} and current density (J_{sc}) declines indicated degradation [34]. TRPL measurements under similar conditions could disentangle these effects by isolating true carrier lifetime changes from capacitance influences, supporting the need for stable measurement conditions to ensure reliable data. Encapsulated devices, which maintained stable V_{oc} , provided more accurate lifetime assessments, highlighting TRPL's role in quality control during stability studies.

Moreover, TRPL's sensitivity to excitation fluence enables the study of carrier density-dependent recombination, a key deter-

minant of V_{oc} . In Sn halide PSCs, high defect densities often linked to V_{Sn} or oxidation accelerate non-radiative recombination at low carrier densities, reducing V_{oc} . Abudulimu et al. demonstrated that TRPL at varying fluences can map this transition, with radiative recombination dominating at higher densities ($n > 1 \times 10^{14} \text{cm}^{-3}$), offering a pathway to optimize material quality for higher V_{oc} . This capability positions TRPL as an essential tool for tailoring processing techniques and passivation strategies (Section 4) to minimize trap states. Future advancements in TRPL, such as in situ measurements during device operation or integration with spatial mapping, could further enhance its resolution, offering deeper insights into V_{oc} enhancement pathways for Sn halide PSCs.

Sun et al. [36] reported pronounced PL quenching and reduced TRPL lifetimes (0.85 ns) in perovskite films coated with trans-3 fullerene, which was attributed to expedited extraction of photogenerated electrons into the ETL. This accelerated extraction diminishes carrier accumulation and interfacial recombination. Importantly, device EL was quantitatively assessed by measuring the external EL quantum efficiency ($Q_{\text{e}}^{\text{lum}}$), which was subsequently converted to non-radiative voltage loss ($\Delta V_{\text{oc}}^{\text{nrad}}$) using the standard reciprocity relation $\Delta V_{\text{oc}}^{\text{nrad}} = -(k_{\text{B}}T/q) \cdot \ln(Q_{\text{e}}^{\text{lum}})$. Devices incorporating trans-3 fullerene exhibited the highest EL intensity (largest $Q_{\text{e}}^{\text{lum}}$) and the lowest calculated $\Delta V_{\text{oc}}^{\text{nrad}}$ (218 mV), consistent with their superior V_{oc} (~ 0.90 V) and FF (~ 0.75) (Figure 5F,G). Dong et al. [37] utilized EL to demonstrate that controlled crystallization reduces trap density, thereby enhancing V_{oc} . Films treated with hexylammonium acetate (HAAc) displayed stronger steady-state PL, and perovskite light-emitting diode (PeLED) devices (ITO/PEDOT:PSS [~ 10 nm]/perovskite [~ 80 nm]/TPBi [40 nm]/LiF [1 nm]/Al [100 nm]) exhibited improved EL characteristics, including higher radiance at lower current densities. These observations indicate reduced trap-assisted recombination and diminished dark current in completed devices (Figure 5H,I). Collectively, these spectroscopic analyses confirm that the primary factors contributing to improvements in V_{oc} and FF are the effective reduction of active trap states.

3.2 | KPFM for Surface Potential Mapping

KPFM is a nanoscale technique that maps surface potential to reveal work function variations, charge distribution, and defect states influencing V_{oc} in PSCs. By measuring contact potential difference (CPD), KPFM helps identify recombination losses and energy misalignments linked to V_{oc} limitations.

KPFM operates in a two-pass mode: first acquiring topography via tapping mode, then lifting the tip to measure CPD by nullifying the electrostatic force through an applied DC bias. This technique is particularly valuable for Sn halide PSCs, where surface defects and oxidation can create potential barriers that reduce V_{oc} . Wang et al. employed KPFM with atomic force microscopy (AFM) to characterize FASnI₃ films doped with phenylhydrazine hydrochloride (PhNHNH_3Cl) and Br^- (denoted PHCl-Br), achieving a PCE of 13.4% and V_{oc} of 0.81 V [38]. Their surface potential mapping showed that PHCl doping increased the chemical potential, suppressing Sn^{2+} oxidation, whereas Br^- incorporation had minimal impact on potential but enhanced film stability.

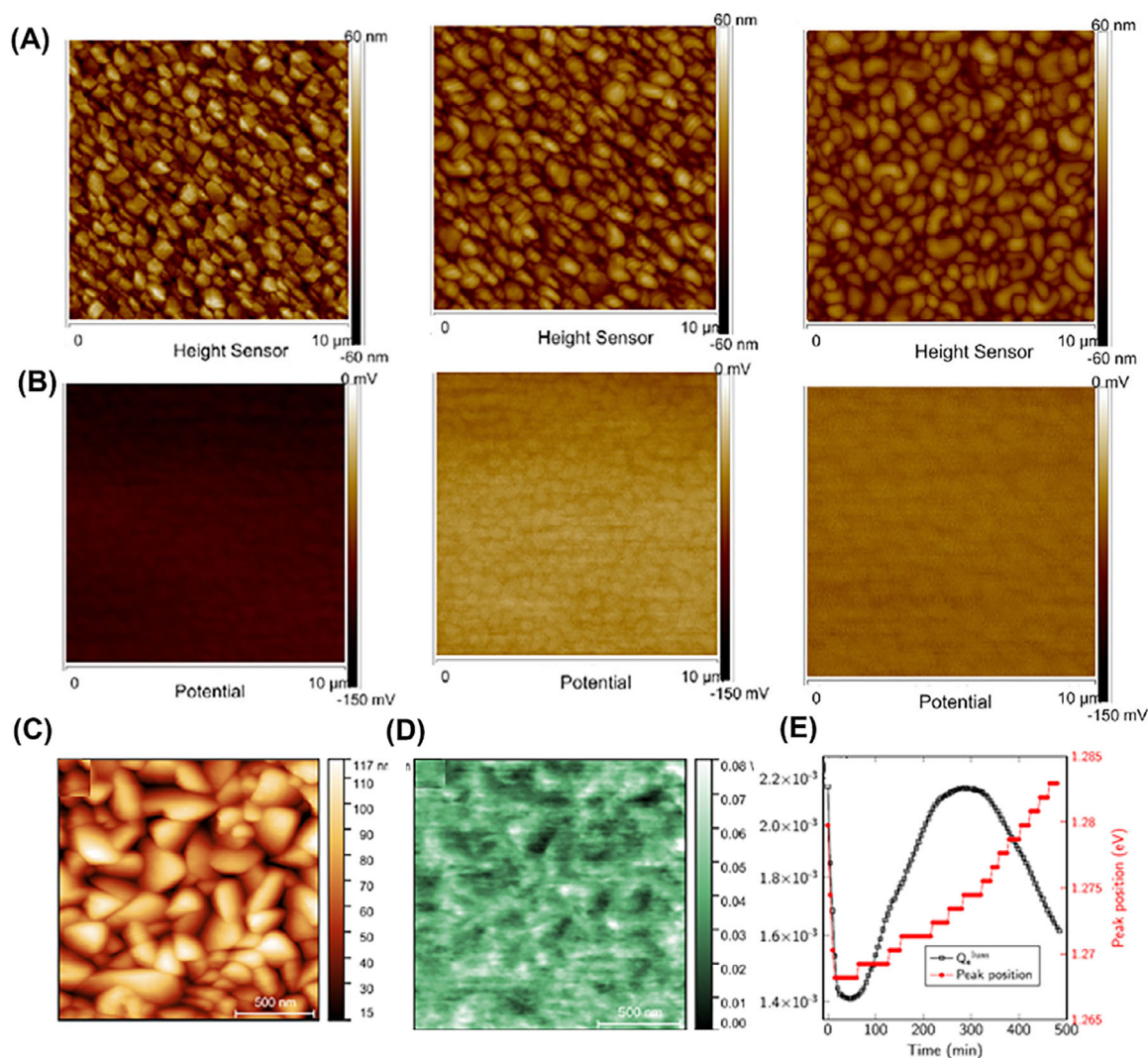


FIGURE 6 | (A) AFM and (B) KPFM micrographs of perovskite, perovskite with PHCL, and PHCL-Br. (C) AFM and (D) CPD mapping of physical vapor deposition (PVD) grown $\text{CH}_3\text{NH}_3\text{SnI}_3$ perovskite, (E) PLQY and PL peak at various time intervals under continuous illumination. Source: (A and B) Reproduced with permission [38]. Copyright 2021, Elsevier. (C–E) CC-BY 4.0 [40] Copyright 2022, American Chemical Society.

The root-mean-square (RMS) roughness decreased from 18.4 nm (pristine FASnI_3) to 10.5 nm (PHCL-Br), correlating with reduced trap states and improved V_{oc} , as smoother surfaces minimize recombination sites (Figure 6A,B). This demonstrates KPFM's ability to link surface potential uniformity to V_{oc} enhancement through defect passivation.

Similarly, Pathak et al. reviewed KPFM applications across perovskite systems, emphasizing its role in probing GBs and their impact on V_{oc} . In Sn halide PSCs, GBs are critical due to their susceptibility to ion migration and degradation, which intensifies non-radiative recombination. Although their study focused primarily on Pb-based perovskites (e.g., $\text{CH}_3\text{NH}_3\text{PbI}_3$), the principles extend to Sn halide systems. For instance, they noted that GBs often exhibit higher CPD under illumination, indicating charge accumulation that can either enhance carrier separation or increase recombination, depending on defect density [39]. Applying this to Sn halide PSCs, KPFM could reveal how strategies like halogen doping (e.g., Cl^- and Br^- in PHCL-

Br modify GB potential, potentially mitigating V_{loss} by stabilizing the lattice and reducing trap states [38].

KPFM's utility in assessing V_{oc} potential is further highlighted by its application to Sn oxidation states and film quality. Singh et al. used KPFM under ultrahigh vacuum (UHV) to study co-evaporated $\text{CH}_3\text{NH}_3\text{SnI}_3$ (MASI) films, confirming Sn exclusively in the +2 oxidation state via x-ray photoelectron spectroscopy (XPS) [40]. Their KPFM measurements revealed a uniform surface potential with variations of only 80 meV across grains (~ 200 nm), with no significant contrast at GBs, suggesting minimal defect-induced recombination sites. This homogeneity, linked to the absence of Sn^{4+} , correlated with high PL quantum yields (PLQY up to 1.6×10^{-3}) and QFLS exceeding 850 meV, indicating a V_{oc} potential approaching 20% PCE if paired with suitable extraction layers (Figure 6C–E). This underscores KPFM's role in verifying material stability and its impact on V_{oc} , complementing TRPL's lifetime data by providing spatial context.

Horn and Schlettwein extended KPFM's application to interface analysis in Sn halide PSCs, investigating FASnI₃ with C₆₀ as the ETL. At low deposition rates, KPFM revealed inhomogeneous C₆₀ growth, with agglomerates at GBs and partial perovskite coverage, yielding two distinct work function components (4.25 eV for a C₆₀ monolayer, 4.37 eV for agglomerates). Higher deposition rates achieved uniform coverage, showing a single work function peak and an extended space charge layer (>90 nm) in C₆₀, with upward band bending indicative of iodide migration [41]. This migration, also observed via XPS, doped C₆₀, reducing interfacial recombination and boosting V_{oc} , consistent with Jiang et al.'s findings of improved V_{oc} (0.94 V) using alternative ETLs like ICBA. KPFM thus elucidates how interface engineering mitigates V_{loss} by optimizing charge extraction and reducing recombination.

KPFM's sensitivity to illumination effects further enhances its utility for V_{oc} analysis. In Wang et al.'s study, the PHCl-Br film's improved surface potential under ambient conditions suggested better charge extraction, corroborated by a five-fold increase in TRPL lifetime (45.5 vs. 9.4 ns for pristine FASnI₃) [38]. This aligns with Pathak et al.'s observation that surface photovoltage (SPV; the CPD difference between dark and light) reflects charge separation efficiency [39]. For Sn halide PSCs, where oxidation-induced defects lower V_{oc} , KPFM's ability to map SPV spatially can pinpoint regions of inefficient carrier transport, as seen in Singh et al.'s stable MASI films under light exposure [40]. This capability guides interfacial optimization, enhancing V_{oc} stability and performance.

Moreover, KPFM complements TRPL by providing spatial context to recombination dynamics. Although Abudulimu et al. used TRPL to quantify carrier lifetimes in Sn-Pb PSCs [34], KPFM could map where these processes dominate, for example, at GBs or grain interiors. Pathak et al. reported that in Pb-based systems, GBs often show higher CPD under bias, suggesting ion migration or defect accumulation [35]. In Sn halide PSCs, KPFM's uniform potential in MASI films explains why longer carrier lifetimes coexist with lower V_{oc} , potentially due to shallow defects altering surface potential [40].

KPFM is essential for evaluating stability in Sn halide PSCs. Wang et al. linked uniform surface potential in PHCl-Br films to suppressed phase segregation and 82% V_{oc} retention after 330 h [38]. Horn and Schlettwein found that iodide migration into C₆₀, though initially beneficial, can degrade long-term performance [41]. In conclusion, KPFM's surface potential mapping is a vital tool for analyzing V_{oc} limitations in Sn halide PSCs, offering spatial resolution to complement TRPL's temporal insights.

3.3 | IS and Recombination Kinetics Analysis

IS is a versatile electrochemical technique that probes the electrical response of materials and devices under an alternating current perturbation, offering profound insights into recombination kinetics and charge transport dynamics that govern V_{oc} in Sn halide PSCs. By analyzing the frequency-dependent impedance, IS unravels the contributions of bulk and interfacial processes, directly linking to the non-radiative recombination and defect states that limit V_{oc} (Section 2). This section reviews how IS

has been applied to Sn halide PSCs to elucidate recombination mechanisms, drawing on recent studies highlighting its role in diagnosing and optimizing device performance.

Kumar et al. employed IS via one-dimensional solar cell capacitance simulator (SCAPS-1D) simulations to study a lead-free MASnI₃-based PSC, observing semicircular Nyquist plots that declined with increasing forward bias from 0 to 1 V, as depicted in Figure 7A [42]. This behavior indicated enhanced carrier conductivity and reduced impedance under forward bias, attributed to improved charge carrier injection that mitigates recombination losses. The semicircular nature confirmed the dominance of the space charge region, a critical factor in V_{oc} determination, as it modulates the depletion region capacitance. Their analysis further showed an exponential rise in capacitance under forward bias, suggesting diffusion capacitance contributions from deep defects near the MASnI₃/Spiro-OMeTAD interface, which aligns with the trap-assisted recombination challenges outlined.

The frequency-dependent nature of IS enables the separation of recombination kinetics across different timescales. Chowdhury et al. utilized IS to assess trap density in FASnI₃-based PSCs passivated with HaHc [43]. They observed a lower capacitance at low frequencies (<10⁵ Hz) in HaHc-doped devices (1.90 ns carrier lifetime) compared to pristine FASnI₃ (1.33 ns), indicating reduced defect states. This reduction correlated with a significant V_{oc} increase from 0.437 to 0.676 V (Figure 7B,C), reflecting suppressed non-radiative recombination due to hydrogen-bonding and Cl⁻ coordination with Sn ion vacancies. The admittance spectra highlighted a transition from trap-dominated to diffusion-limited regimes at higher frequencies, underscoring IS's ability to identify defect contributions to V_{loss} . This complements TRPL findings, where longer carrier lifetimes in passivated films similarly indicated reduced recombination, reinforcing IS as a diagnostic tool for recombination kinetics.

IS also elucidates interfacial effects on V_{oc} , particularly at the ETL/perovskite interface. Yokoyama et al. investigated FASnI₃ PSCs with varying ETLs (Nb₂O₅, TiO₂, SnO₂) using experimental Nyquist plots under short-circuit conditions in the dark [44]. Devices with Nb₂O₅ exhibited lower recombination rates, evidenced by larger semicircle diameters, compared to TiO₂ and SnO₂, correlating with a higher V_{oc} (up to 0.61 vs. 0.42–0.49 V). This was attributed to a near-zero conduction band offset (CBO) of +0.2 eV with Nb₂O₅, reducing the energy difference between the ETL's CBM and the perovskite's VBM to 1.6 eV, thus minimizing interface recombination. In contrast, SnO₂ negative CBO (−1.3 eV) yielded a mere 0.1 eV energy gap, exacerbating recombination and lowering V_{oc} (Figure 7D,E). Simulations further validated this, showing V_{oc} sensitivity to CBO, with optimal values at lower ETL doping concentrations (10¹¹ cm⁻³), highlighting IS's role in optimizing interfacial band alignment for V_{oc} enhancement.

The integration of IS with recombination models, such as SRH, enhances its analytical power. Kumar et al. used SRH recombination to interpret impedance data, linking defect density (10¹⁵ to 10¹⁶ cm⁻³) to V_{oc} deficits [42]. Similarly, Yokoyama et al.'s simulations incorporated SRH theory to correlate CBO-induced recombination rates with experimental V_{oc} trends [44]. These models quantify how trap states mediate carrier loss,

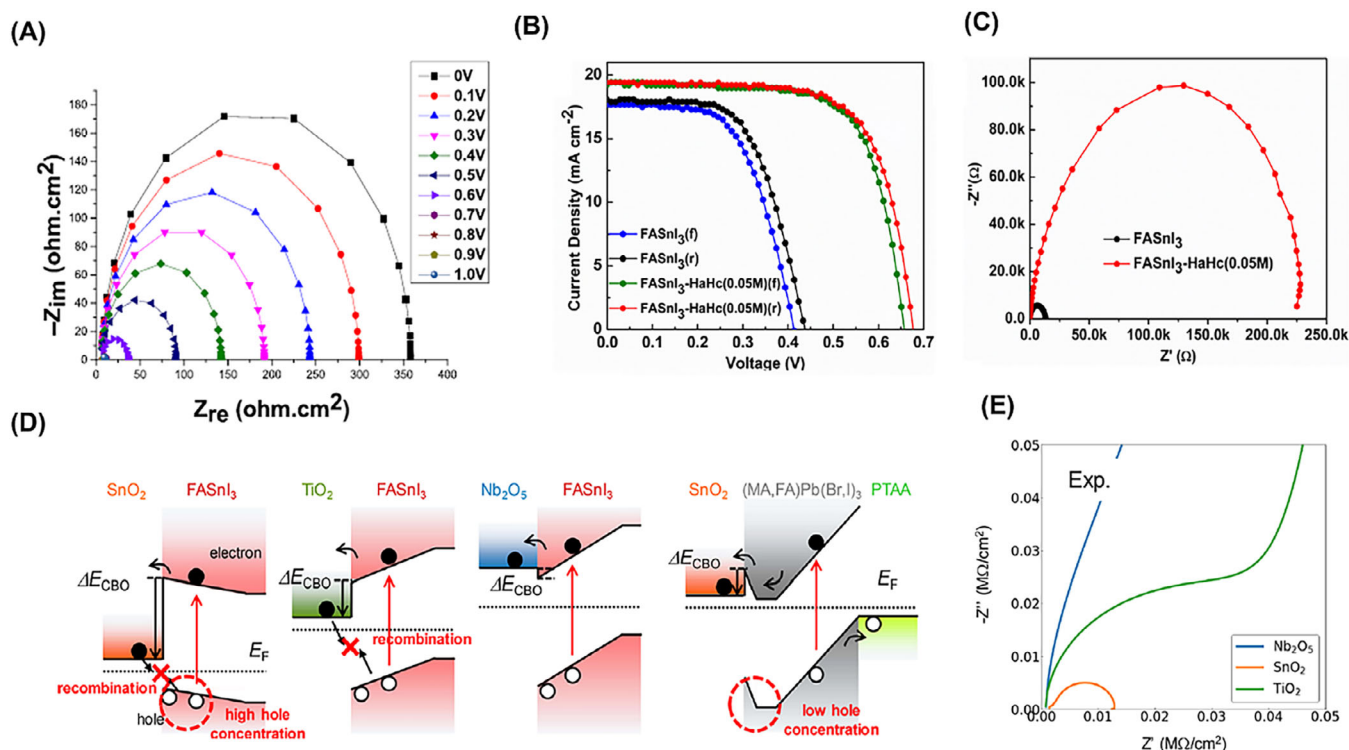


FIGURE 7 | (A) Nyquist curves of MASnI₃ PSCs at different voltages (0–1.0 V). (B) J–V characteristic curves (reverse and forward bias); (C) Nyquist curves for FASnI₃ and FASnI₃–HaHc-based PSCs. (D) Graphical representation of interface band alignments between FASnI₃ with various ETLs and (E) corresponding Nyquist plot behavior of Sn PSCs with different ETLs. Source: (A) Reproduced with permission [42]. Copyright 2022, John Wiley and Sons. (B and C) Reproduced with permission [43]. Copyright 2022, Elsevier. (D and E) Reproduced with permission [44]. Copyright 2020, American Chemical Society.

aligning with Chowdhury et al.'s observation of reduced trap density improving V_{oc} [42]. This synergy between IS and theoretical frameworks bridges empirical data with mechanistic understanding, facilitating targeted V_{oc} optimization strategies.

In summary, IS is a cornerstone technique for analyzing recombination kinetics in Sn halide PSCs, offering detailed insights into bulk and interfacial processes that dictate V_{oc} . Studies like Kumar et al.'s highlight its ability to probe defect-driven recombination [42], whereas Chowdhury et al. demonstrate its sensitivity to passivation effects [43], and Yokoyama et al. underscore its role in interfacial optimization [44]. Future advancements, such as in situ IS under operational conditions or coupling with real-time degradation studies, could further refine its application, enhancing our understanding of V_{loss} mechanisms and supporting the development of high-performance, stable Sn halide PSCs.

3.4 | Drive-Level Capacitance Profiling

DLCP is a depth-sensitive capacitance measurement technique employed to transform capacitance–voltage data into a spatial distribution map of electrically active carriers and trap densities within perovskite films. Jiang et al. [45] utilized DLCP at elevated AC frequencies to compare perovskite films fabricated with various antisolvents. Their findings indicated that films treated with dichlorobenzene (DCB) exhibited the lowest overall carrier density throughout the profiling depth, which was attributed to

enhanced charge transport efficiency within the perovskite layer. Given that elevated local carrier densities at the ETL/perovskite interface can exacerbate interfacial recombination and leakage currents, these DLCP results have been interpreted as direct evidence that the DCB treatment effectively mitigates self-doping and eliminates interface trap states (see Figure 8A,B).

In a related study, Jin et al. [46] employed DLCP to monitor trap and carrier density profiles before and after light-induced aging. Their results demonstrated that the control samples exhibited an accumulation of traps over time, whereas samples treated with 4-mercaptobenzoic acid (4-MBA) maintained essentially stable DLCP profiles and integrated trap densities. This observed stability in trap profiles, as measured by DLCP, corresponded with consistent trap density of states (tDOS) measurements. As open-circuit voltage (V_{oc}) degradation and FF decline under operational conditions are primarily driven by trap accumulation, DLCP provided direct evidence that the regenerative redox approach utilizing 4-MBA effectively inhibits trap formation (refer to Figure 8C,D). Furthermore, DLCP measurements revealed that the incorporation of thiosulfate ($S_2O_3^{2-}$) as an additive in perovskite films led to a reduction in defect density throughout the film relative to control samples [47]. Because a uniform decrease in trap density implies a reduction in deep traps available for SRH recombination within the absorber layer and fewer trap-assisted leakage pathways at interfaces, these DLCP findings were employed to rationalize the significantly diminished tDOS inferred from thermal conductivity spectra (see Figure 8E,F).

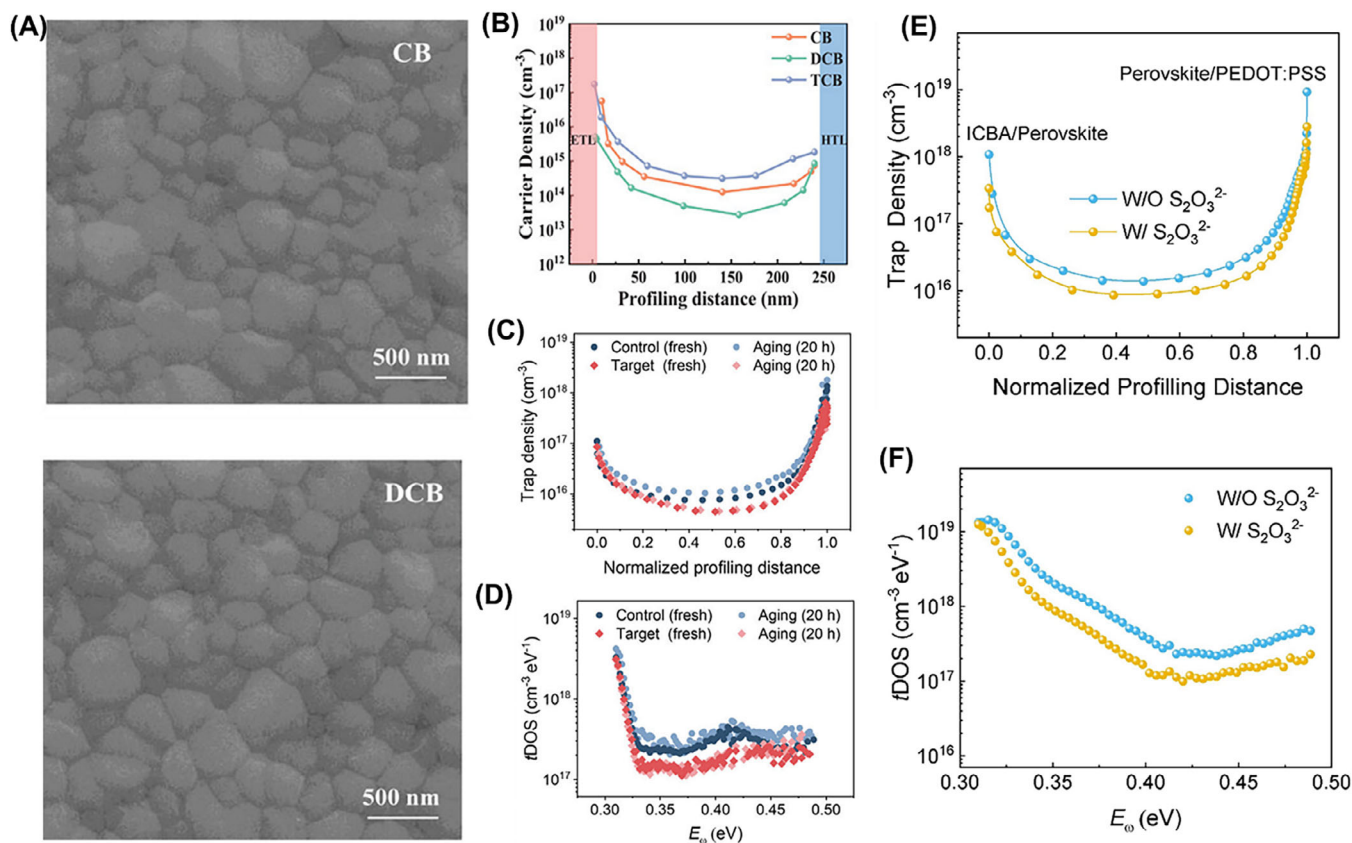


FIGURE 8 | (A and B) SEM micrographs of perovskite films treated with chlorobenzene (CB) and dichlorobenzene (DCB), spatial distribution of carrier density obtained through drive-level capacitance profiling (DLCP) for CB-, DCB-, and trichlorobenzene (TCB)-treated perovskite films. (C and D) DLCP and tDOS profiles of 4-MBA-based PSC before and after the aging process. (E and F) DLCP and tDOS characteristic profiles of Sn perovskite devices without and with thiosulfate additive. tDOS, trap density of states. Source: (A and B) Reproduced with permission [45]. Copyright 2025, John Wiley and Sons. (C and D) Reproduced with permission [46]. Copyright 2025, John Wiley and Sons. (E and F) Reproduced with permission [47]. Copyright 2024, John Wiley and Sons.

3.5 | TAS Analysis

TAS is a capacitance–frequency measurement technique that varies with temperature and is utilized to determine the activation energy (E_a) associated with ion migration in PSCs. In studies involving SnX₂ additives, two distinct E_a values were identified in the FASnI₃ device, specifically at 1.05 and 0.24 eV, which have been attributed to tin vacancy (V_{Sn}) and iodine vacancy (V_I) defects, respectively. Upon incorporation of SnF₂ into the FASnI₃ device, the E_a increased to 1.33 eV, suggesting a suppression of the mobility of the predominant ionic species (Figure 9A–D). Conversely, the addition of SnBr₂ resulted in a considerably lower E_a of 0.79 eV. These findings indicate that SnF₂ elevates the energy barrier for defect species responsible for self-p-type doping and recombination processes, thereby playing a critical role in enhancing the open-circuit voltage (V_{oc}) [48].

Zhou et al. [49] employed TAS to extract the tDOS in both pristine FASnI₃ and 2,8-dibromo-dibenzothiophene-S,S-dioxide (BrDS)-doped FASnI₃ PSCs. Their results demonstrated a marked reduction in trap-assisted non-radiative recombination in the BrDS-doped samples, which corresponded to improved device performance, with V_{oc} increasing to approximately 0.78 V and FF reaching 76.31%, compared to the control devices exhibiting V_{oc} of approximately 0.69 V and FF of 70.79% (Figure 9E–G).

Furthermore, Teng et al. [50] combined deep-level capacitance profiling (DLCP) with TAS to investigate the spatial distribution of trap densities within PSCs. Their analysis revealed that the trap density at the surface remained comparable between control and F3-TMOS-modified films, whereas a significant reduction in trap density was observed near the bottom interface in the F3-TMOS-modified films. This reduction was attributed to effective defect passivation at the buried interface. TAS measurements identified multiple trap bands (I–III) at energies of 0.33, 0.38, and 0.47 eV, respectively, with the deepest traps (Band III) localized predominantly at the perovskite/HTL interface. Notably, the buried-interface modification led to a decrease in the density of these deep-interface traps, as evidenced in Figure 9H,I.

3.6 | ML/AI Insights Into V_{loss} Mechanisms

ML and AI are proving to be game-changers in overcoming the core challenges of Sn halide PSCs, especially when it comes to boosting their V_{oc} . Although these Pb-free alternatives are environmentally favorable, they are hindered by issues like the easy oxidation of Sn²⁺, uncontrollable crystallization rates, and defect-related recombination losses, all of which constrain V_{oc} and limit device efficiency. Relying on conventional trial-and-error techniques is both costly and slow, underscoring

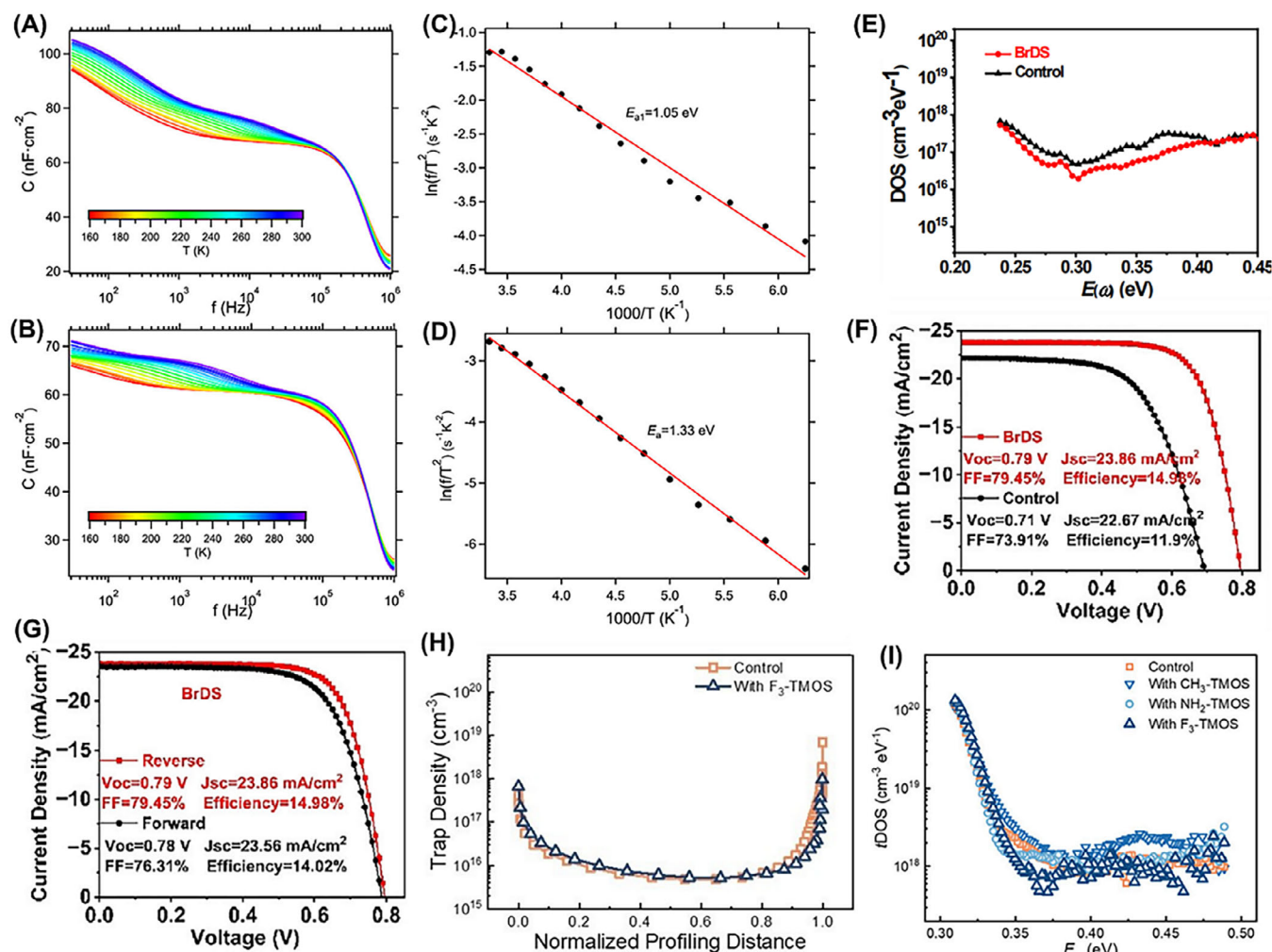


FIGURE 9 | (A–D) Capacitance–frequency characteristics obtained from TAS measurements for FASnI₃ and (B) FASnI₃ + SnF₂ devices under dark conditions (temperature 160–300 K) at 0 V DC bias with an AC modulation (amplitude ~10 mV). Ionic defect activation energy for (C) FASnI₃ and (D) FASnI₃ + SnF₂ extracted from the Arrhenius plots. (E) tDOS of control and BrDS-doped FASnI₃ perovskite device, forward and reverse bias scanned *J*–*V* characteristic curves of (F) FASnI₃ and (G) BrDS-doped FASnI₃ PSCs. (H and I) Charge carrier density profile (DLCP) and tDOS for perovskite films without and with F₃-TMOS modification. *Source:* (A–D) Reproduced with permission [48]. Copyright 2024, American Chemical Society. (E–G) Reproduced with permission [49]. Copyright 2024, Royal Society of Chemistry. (H and I) Reproduced with permission [50]. Copyright 2024, John Wiley and Sons.

the growing need for smarter, predictive strategies driven by advanced algorithms. This sub-section underscores the ML and AI insight into the V_{loss} mechanism and analysis.

Studies demonstrate ML's efficacy in optimizing device parameters and predicting performance outcomes. Hasanazadeh Azar et al. [51] demonstrated the utility of ML combined with SCAPS-1D for the predictive design of PSCs, determining optimal hole transport and active layer combinations for maximizing V_{oc} . Their predictive models yielded highly accurate performance forecasts, enabling precise optimization strategies tailored for enhanced V_{oc} in Sn halide perovskites. By training ML models on experimental datasets, including E_g , highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) offsets ($\Delta H/\Delta L$) and device outputs (V_{oc} , J_{sc} , FF, PCE), researchers can reveal hidden correlations that govern V_{oc} behavior, which are otherwise difficult to identify through traditional methods.

ML and AI significantly contributed to mitigating the V_{loss} in Sn halide PSCs by enabling a data-driven optimization of both material composition and interfacial energy alignment. Using artificial neural network (ANN) models trained on literature-based experimental datasets, Gao et al. [52] predicted that a wide E_g (~1.6 eV) perovskite combined with minimal interfacial energy offsets (ΔHOMO and $\Delta \text{LUMO} < 0.15$ eV) would yield high V_{oc} values (up to 1.28 V). The ML model also identified ΔHOMO as the most critical factor influencing V_{oc} , providing targeted insight into interface engineering. This allowed rational material selection (e.g., FA_{0.8}MA_{0.2}Sn(Br_{0.3}I_{0.7})₃) and device design without relying on trial-and-error, ultimately leading to reduced non-radiative recombination and suppressed V_{oc} deficit (Figure 10A,B). Their model indicated that optimizing energy-level alignment at interfaces significantly enhances V_{oc} and device stability, providing practical guidance for exceeding 20% efficiency in Sn halide PSCs.

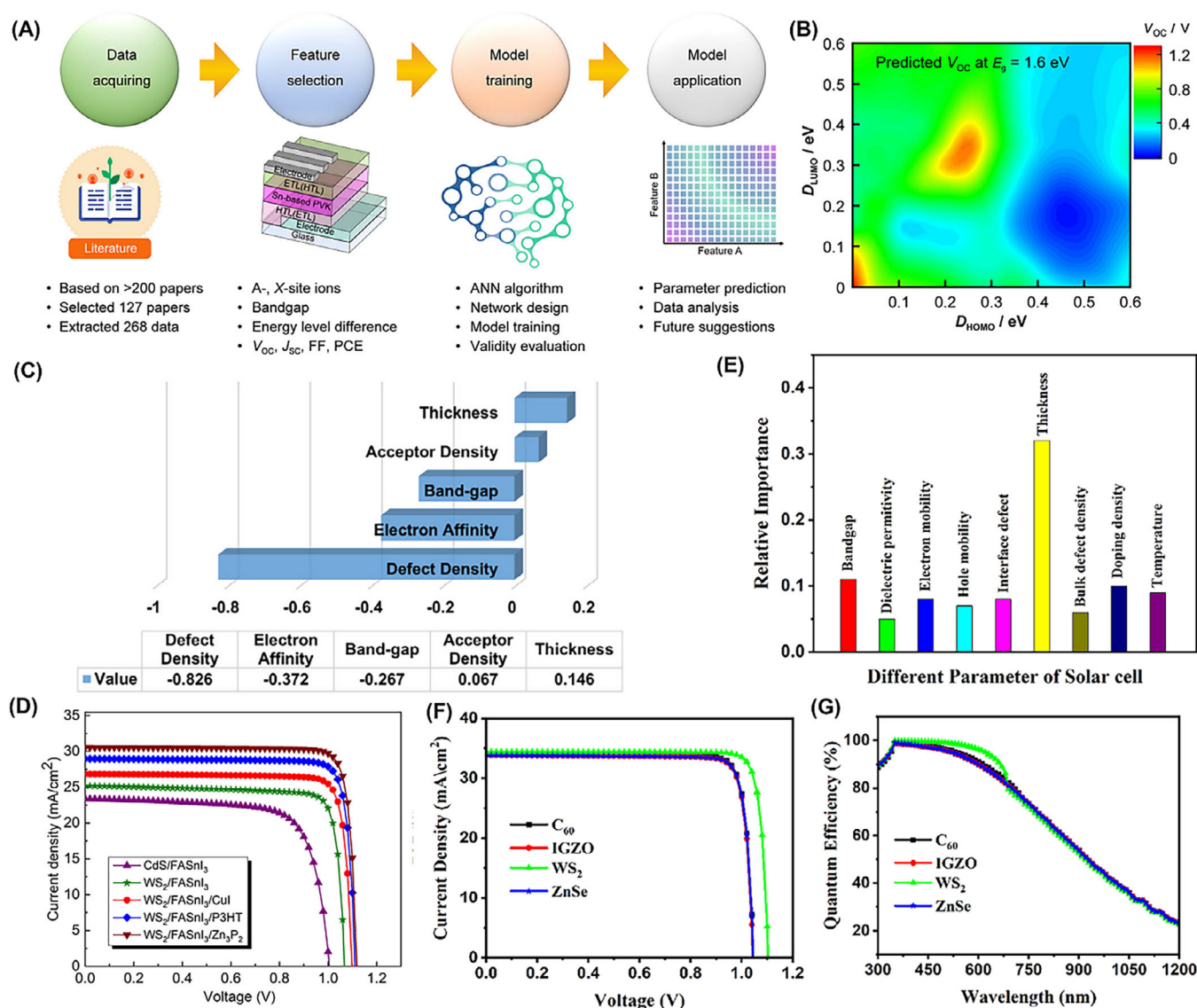


FIGURE 10 | (A) Graphical representation of ML using an ANN model, (B) 4D scatter plots of anticipated V_{oc} by setting $E_g = 1.4$ eV. (C and D) Predicted influence of input parameters on efficiency and $J-V$ characteristic prediction of FASnI₃ PSCs without HTL and with various HTLs. (E–G) The ML model determines several crucial parameters that govern the optimized performance of FTO/WS₂/MASnBr₃/V₂O₅/Au PSCs, corresponding $J-V$ curves, and quantum efficiency analysis of MASnBr₃ PSC with various ETLs. ANN, artificial neural network; FF, fill factor; PCE, power conversion efficiency. *Source:* (A and B) Reproduced with permission [52]. Copyright 2024, Springer Nature. (C and D) Reproduced with permission [53]. Copyright 2024, John Wiley and Sons. (E–G) Reproduced with permission [54]. Copyright 2025, John Wiley and Sons.

Khan and Ahmed [53] further illustrated the potential of ML in evaluating the influence of various physical parameters, including defect densities and interface qualities, on V_{oc} in FASnI₃-based PSCs. A supervised ML model, a multiple linear regression (MLR) algorithm, was trained on a dataset generated by SCAPS-1D simulations covering layer thickness, E_g , electron affinity, doping density, and defect density variations. The ML analysis revealed that defect density had the strongest negative correlation with device efficiency, indicating it as the dominant factor limiting V_{oc} . Using this insight, the study reveals the optimization of the absorber layer to a defect density of 10^{15} cm⁻³ and interface defect states to 10^{11} cm⁻², significantly reducing non-radiative recombination and enabling a high V_{oc} of 1.12 V, which is exceptionally close to the theoretical limit for the 1.41 eV

E_g of FASnI₃ (Figure 10C,D). By prioritizing defect control based on ML output, the device achieved a PCE of 29.81%.

Moreover, in a very recent study, ML was used to optimize the PV performance of lead-free CH₃NH₃SnBr₃-based PSCs with a particular focus on mitigating V_{loss} . Using a random forest algorithm (RFA), critical device parameters, including absorber thickness, interface defect density, and doping level, were identified that significantly influence V_{oc} and overall efficiency. By integrating ML with SCAPS-1D simulations, they systematically optimized the absorber and CTLs to minimize recombination and improve charge extraction. This led to a predicted V_{oc} of up to 1.10 V and a PCE exceeding 33% for the optimized WS₂-based configuration. Collectively, these studies emphasize ML

and AI as essential in overcoming the efficiency bottlenecks in Sn halide PSCs, particularly in enhancing V_{oc} (Figure 10E–G). ML-driven strategies provide a systematic approach for predicting and optimizing critical device parameters, significantly accelerating experimental workflows, reducing costs, and paving the way for more stable and efficient Sn halide PSCs [54].

4 | Strategies for Enhancing V_{oc} in Sn Halide PSC

Enhancing the V_{oc} and FF remains a central challenge in advancing Sn halide PSCs, primarily due to their susceptibility to defect-induced non-radiative recombination, intrinsic p-type self-doping, and Sn oxidation. This section outlines key strategies aiming at overcoming these limitations, including molecular defect passivation, compositional engineering, crystallization control, and interface optimization, each contributing to improved electronic properties.

4.1 | Processing and Crystallization Control

The V_{oc} and FF in Sn halide PSCs are the key factors influencing PCE but are often constrained by rapid crystallization, defect formation during film deposition, and Sn^{2+} oxidation. Advancements in processing techniques, especially solvent, antisolvent, and additive engineering, have shown promise in improving film quality, suppressing defects, and enhancing V_{oc} , FF, and efficiency of the device. This section highlights the role of antisolvent and additive strategies in optimizing crystallization dynamics and boosting device performance [55]. The commonly employed polar solvent DMSO oxidizes Sn^{2+} to Sn^{4+} and promotes uncontrolled nucleation, resulting in polycrystalline films characterized by high defect densities and self-induced p-type doping, which adversely affect both the V_{oc} and FF. In a comprehensive study, Di Girolamo et al. [56] screened over 2000 solvents and identified novel nonsulfoxide, non-oxidizing solvents capable of forming stable FASnI_3 precursor solutions without inducing Sn^{2+} oxidation. Specifically, the optimized solvent mixture of *N,N*-diethylformamide and *N,N*-dimethylpropyleneurea (DEF:DMPU) effectively minimized oxidation-related trap states and facilitated slower, more uniform film growth. The resultant films exhibited enhanced crystallinity, achieving improved device performance metrics with V_{oc} approximately 0.55 V, FF around 53%, and PCE near 6.2%, in contrast to DMSO-processed films, which showed V_{oc} of about 0.49 V, FF of 52%, and efficiency of 3.84%. These findings underscore the critical importance of solvent stability and controlled crystallization kinetics in the fabrication of efficient tin halide perovskite devices (see Figure 11A,B).

FASnI_3 is commonly synthesized using a one-step antisolvent-assisted technique, wherein the antisolvent plays a critical role in controlling crystallization and determining the quality of the resulting film. Conventionally, DMSO, a polar solvent characterized by a high donor number and low vapor pressure, has been employed. However, typical antisolvents such as chlorobenzene (CB), which possess a lower donor number, often fail to completely extract DMSO, leading to residual excess DMSO within the perovskite film. In a study by Zhang et al. [57], CB was partially substituted with DMS to form a mixed

antisolvent system (CB:DMS = 6:1). DMS, exhibiting both a high donor number and high vapor pressure, facilitated more effective extraction of DMSO and promoted uniform nucleation. This optimized crystallization approach produced smooth and compact films with reduced defect densities, decreasing from $1.04 \times 10^{17} \text{ cm}^{-3}$ in the control sample to $8.42 \times 10^{16} \text{ cm}^{-3}$ in the CB:DMS (6:1) treated films. Consequently, enhancements in device performance were observed, with the V_{oc} increasing from 0.39 to 0.44 V and the FF improving from 58.3% to 61.6% (see Figure 11C,D).

Moreover, CB's toxicity limits the environmental appeal of Sn halide PSCs. Recent research has shifted toward greener antisolvents to balance performance and sustainability. Zhang et al. [55] introduced diethyl carbonate (DEC) as an environmentally friendly alternative, demonstrating its ability to retard solvent–antisolvent interaction kinetics compared to CB. A standout feature of DEC processing is its regulation of p-type self-doping, a common issue in Sn halide perovskites due to V_{Sn} . Excessive p-doping increases carrier concentration and shifts the Fermi level toward the VB. It is investigated that in DEC-processed FASnI_3 films, the gradient distribution of p-type doping causes band-bending downward at the top surface and upward at the bottom. This built-in potential will likely enhance charge carrier separation, endorse carrier extraction, and suppress reverse charge accumulation at the interface, thereby mitigating non-radiative recombination associated with bulk defects. KPFM and ultraviolet photoelectron spectroscopy (UPS) to demonstrate that DEC treatment reduces the surface work function from 4.49 to 4.31 eV, indicating suppressed p-type character near the perovskite/ C_{60} interface (Figure 11E,F). Cross-sectional KPFM further revealed a vertical potential gradient across the film, with increasing p-type doping from the upper to the lower regions, highlighting spatial inhomogeneity in defect distribution.

Su et al. [58] demonstrated that uncontrolled crystallization in tin-based perovskites results in the formation of pinholes, cracks, and a high density of defects, which generate deep traps and tin vacancies. These structural imperfections promote non-radiative recombination and shunting pathways, significantly reducing the open-circuit voltage (V_{oc}) and FF. By incorporating acetic acid (HAc) into the precursor solution, the authors established a mildly acidic environment that stabilized Sn^{2+} ions and facilitated hydrogen bonding between HAc and iodide ions (I^-), effectively mitigating iodine loss. The presence of pre-nucleated clusters regulated the supersaturation level and lowered the nucleation barrier, thereby producing uniform, pinhole-free films characterized by larger grain sizes and fewer defects. This enhanced morphology diminished trap-assisted recombination, resulting in an increase of V_{oc} to 0.75 V and FF to 74.97%, culminating in a peak PCE of 12.26% (Figure 11G–I).

In the case of CsSnI_3 films, nonuniform crystallization was observed due to the aggregation of the commonly employed additive SnF_2 , which led to rough surface morphology, phase segregation, and elevated trap-mediated recombination, thereby deteriorating V_{oc} and FF. To address these issues, Ban et al. [59] introduced 2-aminopyrazine (APZ) as a co-additive that formed an SnF_2 –APZ complex, promoting homogeneous dispersion of SnF_2 and enabling controlled coordination during crystallization. The amino groups in APZ functioned as Lewis bases, coordinat-

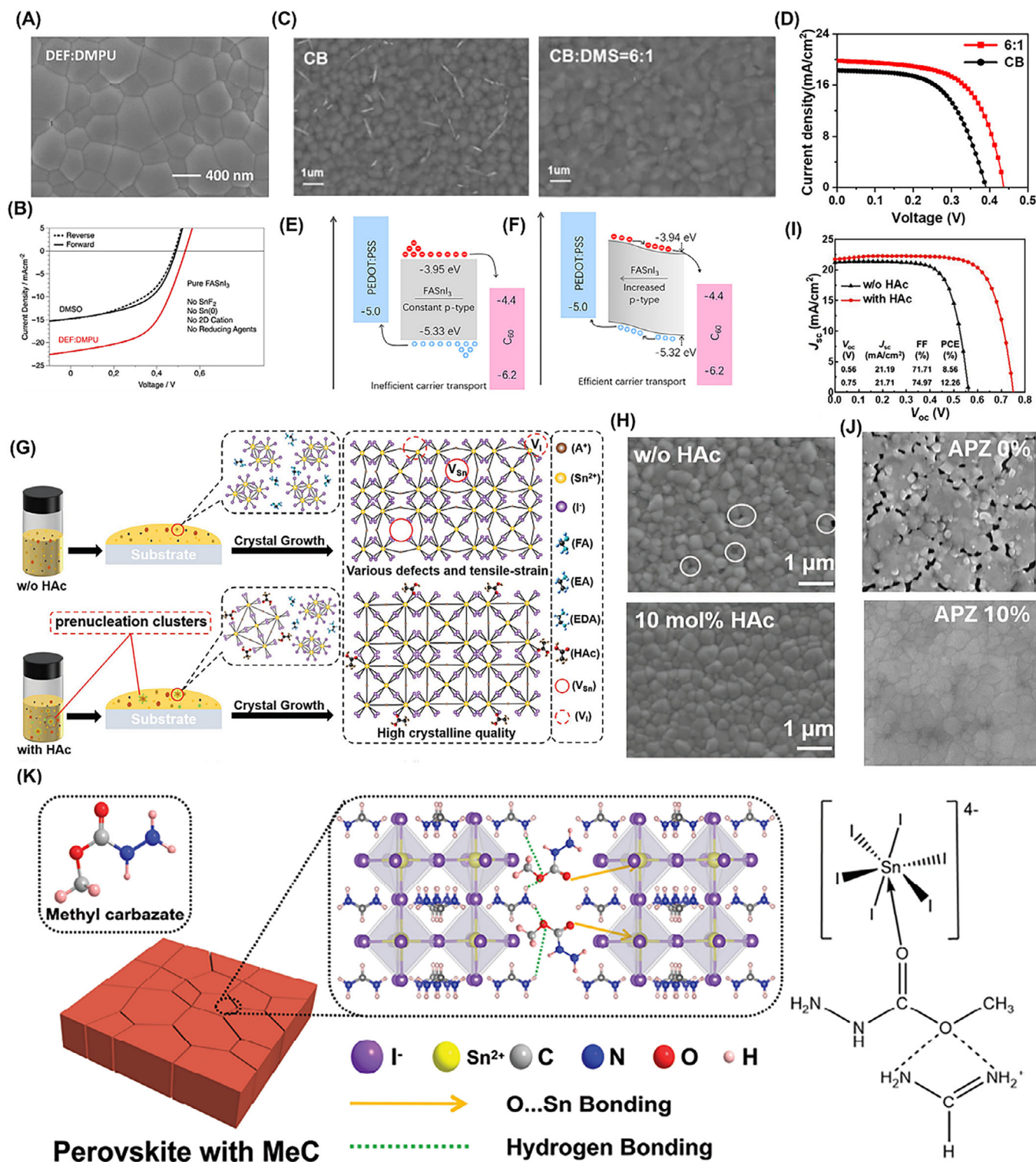


FIGURE 11 | (A) Top view of SEM image for perovskite with DEF:DMPU solvent, (B) J - V characteristic curves for perovskite device with DMSO and DEF:DMPU solvents. (C and D) SEM micrographs and corresponding J - V characteristic curves of PSCs prepared by CB and CB:DMS = 6:1. Energy band diagrams of (E) the control perovskite with CB and (F) DEC antisolvent perovskite-fabricated PSCs. (G-I) Schematic representation of the uncontrolled crystallization process in perovskite films without the addition of HAC, contrasted with the stabilization and regulated crystal growth observed following the incorporation of 10% HAC. Scanning electron microscopy (SEM) images of the perovskite films are provided alongside the corresponding current-voltage (J - V) characteristic curves for perovskite solar cells (PSCs) fabricated without HAC and with 10% HAC. (J) SEM micrographs of 0% APZ CsSnI₃ and 10 mol% APZ added CsSnI₃ perovskite films. (K) Schematic representation of methyl carbazate (MeC) interaction with the perovskite. APZ, 2-aminopyrazine; CB, chlorobenzene; DEF, *N,N*-diethylformamide; DMPU, *N,N*-dimethylpropyleneurea; DMS, dimethyl sulfide; HAC, acetic acid. Source: (A and B) Reproduced with permission [56]. Copyright 2021, American Chemical Society. (C-F) Reproduced with permission [57]. Copyright 2024, Royal Society of Chemistry. Reproduced with permission [55]. Copyright 2023, Royal Society of Chemistry. (G-I) Reproduced with permission [58]. (J) Reproduced with permission [59]. Copyright 2021, John Wiley and Sons. (K) Reproduced with permission [60]. Copyright 2024, John Wiley and Sons.

ing with Sn^{2+} ions to inhibit oxidation and modulate nucleation kinetics, ultimately yielding uniform and compact CsSnI_3 films (Figure 11J).

Yuan et al. [60] identified that the inherently high Lewis acidity of Sn^{2+} induces excessively rapid crystallization, resulting in films with small grains, numerous GBs, and abundant traps that accelerate non-radiative recombination, thereby limiting V_{oc} and FF. To counteract this, they introduced methyl carbazate (MeC) as a multifunctional additive capable of forming intermolecular $\text{O}\cdots\text{Sn}$ coordination bonds and $\text{N-H}\cdots\text{O}$ hydrogen bonds with the perovskite precursors. These interactions served to bridge and stabilize the lattice structure, suppress Sn^{2+} oxidation, and decelerate the crystallization process, facilitating more complete grain growth (Figure 11K). As a result, both V_{oc} and FF exhibited significant improvements, and the PCE increased from 10.43% to 14.02%.

4.2 | Material Engineering Approaches

4.2.1 | Alloying and Compositional Engineering

Alloying Sn with other elements stabilizes the perovskite lattice and reduces Sn^{2+} oxidation to Sn^{4+} , a key contributor to V_{loss} is deep defect densities, self-p-type doping, and Sn^{2+} oxidation, as discussed in the previous section. One effective method involves incorporating trivalent cations like antimony (Sb^{3+}) for counter-doping. For example, adding SbF_3 reduces the hole concentration from 1.79×10^{16} to $6.46 \times 10^{14} \text{ cm}^{-3}$, shifting the Fermi level toward the CBM and increasing carrier lifetime [61]. This strategy effectively passivates deep-level defects, such as V_{I} , by transforming them into shallower states, as DFT calculations confirm. Specifically, Sb^{3+} substitution at Sn^{2+} sites introduces shallow donor-like states (Figure 12A), with charge transition levels supporting its electron-donating behavior. This defect modulation enhances carrier mobility and improves the electronic quality of the perovskite, resulting in a significant increase in V_{oc} from 0.830 to 0.938 V and boosting the PCE to 14.37% [61]. The fluoride anions in SbF_3 also passivate undercoordinated Sn^{2+} sites, leveraging F^- strong electronegativity to suppress oxidation [61]. An alternative strategy eliminates traditional additives like SnF_2 , which can cause phase separation and interfacial impurities (e.g., SnS). Using excess SnI_2 and ethylenediamine dihydroiodide (EDAI_2) in an SnF_2 -free approach enhances film morphology, crystallinity, and stability [62]. For non-stoichiometric $\text{FA}_{0.8}\text{SnI}_{2.8}$ films with 3 mol% EDAI_2 and 25 mol% excess SnI_2 , a steady-state PCE of 10.0% with a V_{oc} of 0.63 V was achieved, alongside improved light stability. This method avoids SnS impurities, reduces trap-assisted recombination, and increases the built-in potential, evidenced by a lower dark current and a carrier lifetime of 2.66 ns compared to 1.66 ns with SnF_2 [62]. A recent study introduced gradient germanium (Ge) doping to create a homojunction structure in Sn halide PSCs, tackling p-type self-doping and carrier recombination to reduce V_{loss} [63]. By incorporating Ge^{2+} ions, which donate electrons and suppress Sn oxidation, a gradient distribution of Ge was achieved, higher at the top surface (8%) and decreasing toward the bottom (2%) of the perovskite film. This gradient doping establishes an internal electric field across the film, reducing dark current by over 2 orders of magnitude (from 1.08×10^{-5} to $6.45 \times 10^{-8} \text{ mA cm}^{-2}$)

and trap density by an order of magnitude (from 1.45×10^{16} to $8.7 \times 10^{15} \text{ cm}^{-3}$). The resultant devices achieved a PCE of 13.3% with a V_{oc} of 0.85 V and demonstrated excellent stability. DFT study revealed (Figure 12B) that Ge doping introduces n-type defects (e.g., Ge replacing FA, denoted Ge_{FA}), counteracting p-type self-doping by donating electrons to V_{Sn} , shifting energy levels upward, and enhancing charge extraction while reducing recombination [63]. This work highlights gradient doping as a novel strategy to enhance V_{oc} in Sn halide PSCs by optimizing spatial energy levels and film quality.

4.2.2 | Dimensionality Control: Two-Dimensional (2D)/3D Heterostructures

Combining 2D and 3D perovskite structures enhances V_{oc} by reducing defect density and non-radiative recombination, leveraging the stability of 2D layers and the charge transport efficiency of 3D structures. Traditional organic spacers such as phenethylammonium (PEA) and butylammonium (BA) form 2D layers at surfaces or GBs, passivating defects and suppressing ion migration [64]. Spacer design is crucial; alicyclic spacers like morpholinium iodide (MP) improve structural rigidity and intermolecular interactions, forming oriented 2D/3D heterostructures with reduced disorder [64]. MP's secondary ammonium and ether groups enhance hydrogen bonding with $[\text{SnI}_6]^{4-}$ octahedra (Figure 12C), lowering Urbach energy from 224.4 to 118.8 meV, resulting in a PCE of 12.04% and a V_{oc} of 0.803 V (vs. 0.596 V for pristine 3D) [64]. The hydrophobic MP layer also boosts oxidative stability, retaining 77% of the initial PCE [64]. Advanced molecular engineering employs fluorinated spacers like 3,5-difluorobenzylamine (DFBA), forming low-dimensional perovskites with a unique two-layer structure (Figure 12D). DFBA's fluorine atoms increase hydrophobicity (contact angle 41.7° vs. 16.8° for 3D) and packing efficiency, reducing Sn^{4+} content from 64% to 12% and passivating Sn vacancies [65]. This yields a PCE of 8.38% and exceptional stability, retaining over 90% efficiency after 10 h of unencapsulated operation in the air. The quasi-2D ($n = 2$) structure minimizes quantum confinement, facilitating charge transport while enhancing stability against water and oxygen, addressing recombination and defect challenges from Section 2. A recent study developed phase-pure 2D/3D tin-based perovskite films using 4,4-difluoropiperidine (DFPD^+) cations to form $\text{DFPD}_2\text{SnI}_4/\text{FASnI}_3$ heterostructures [66]. The DFPD^+ cations, with high positive charge density, are tightly coupled with Sn-I components, promoting the formation of phase-pure 2D/3D films via a one-pot solution process. Good lattice matching between $\text{DFPD}_2\text{SnI}_4$ (lattice constant 12.66 Å along the (0 0 2) plane) and FASnI_3 (6.31 Å along the (1 0 0) plane) regulates crystallization, boosting oriented growth of FASnI_3 (h 0 0) planes, which are optimal for light absorption and carrier transport. The 2D $\text{DFPD}_2\text{SnI}_4$ layers, distributed along GBs, stabilize FASnI_3 grains through hydrogen bonding in the organic spacers, reducing defect generation and enhancing environmental stability. This approach achieved a PCE of 13.34% with a V_{oc} of 0.806 V, alongside improved stability, retaining over 90% of the initial PCE after 200 h at the maximum power point [66]. TRPL showed a longer carrier lifetime (23.88 vs. 15.15 ns for the control), and TAS confirmed reduced trap states, with a lifetime of 1374.1 versus 879.6 ps. This work underscores the

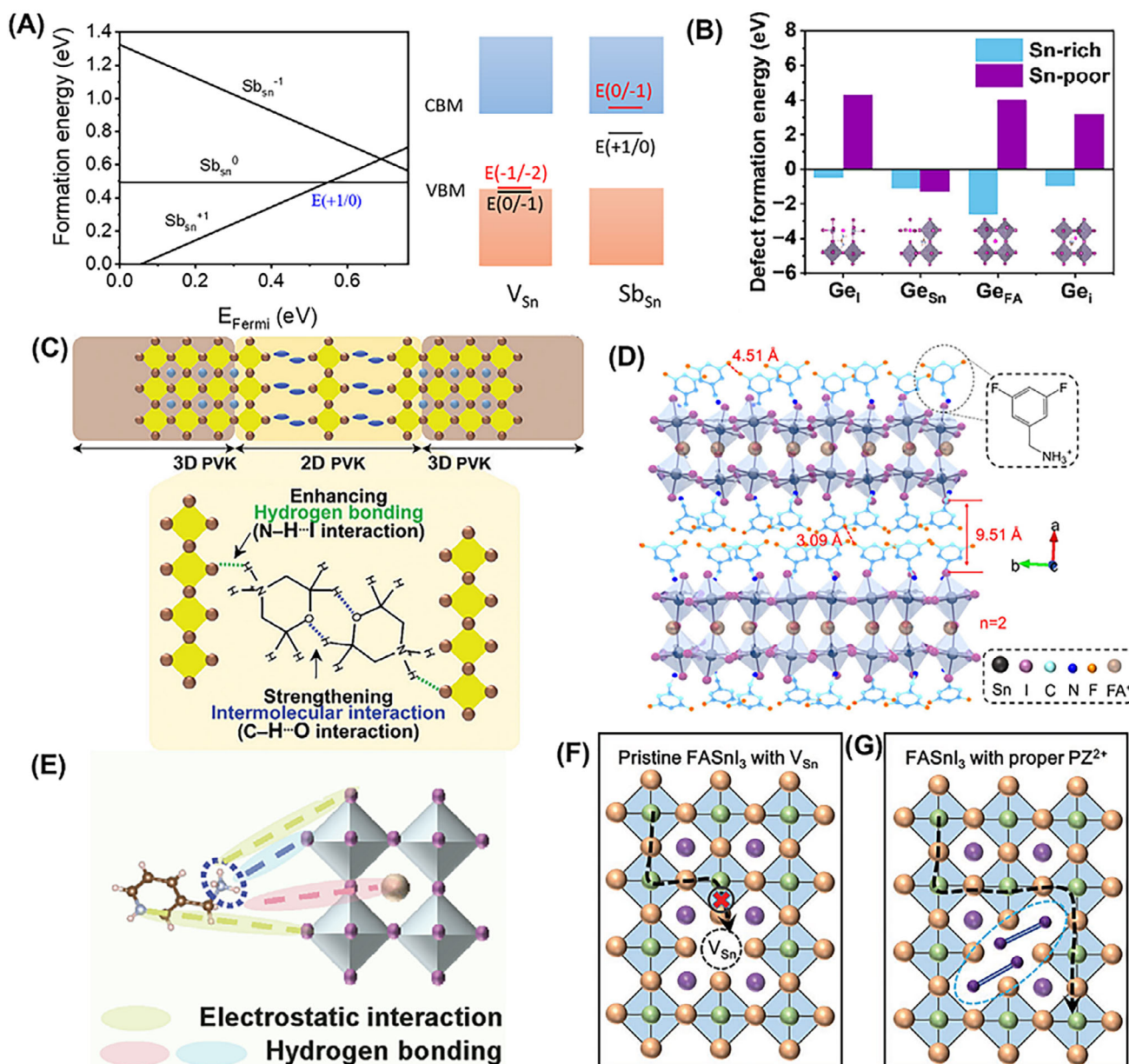


FIGURE 12 | (A) Defect formation energy of Sb_{Sn} with various transition states as a function of Fermi energy in the FASnI_3 supercell. (B) Ge_{FA} , Ge_{Sn} , Ge_{I} , and Ge_{I} defect formation energy diagram calculated from the HSE method. (C) Graphical illustration of morpholinium-based 2D/3D perovskite crystal structure and molecular interactions. (D) Crystal structure and bonding characteristics of $(\text{DFBA})_2\text{FASn}_2\text{I}_7$ ($n = 2$) elucidated using 3,5-difluorobenzylamine (DFBA) as the A-site cation. (E) Graphical illustration of molecular interaction and bonding between 3AMPY²⁺ and 3D components of perovskite. Graphical representation of perovskite crystal structures and associated charge carrier transport routes (F) FASnI_3 and (G) FASnI_3 with piperazine ($\text{FA}_{1-2}\text{PZ}_{2y}\text{Sn}_{1-y}\text{I}_3$). 2D, two-dimensional; 3D, three-dimensional; CBM, conduction band minimum; VBM, valence band maximum. *Source:* (A) CC BY license [61] Copyright 2024, John Wiley and Sons. (B) Reproduced with permission [63]. Copyright 2024, American Chemical Society. (C) CC BY license [64] Copyright 2024, John Wiley and Sons. (D) Reproduced with permission [65]. Copyright 2022, John Wiley and Sons. (E) Reproduced with permission [67]. Copyright 2024, John Wiley and Sons. (F and G) Reproduced with permission [68]. Copyright 2021, John Wiley and Sons.

importance of cation design in achieving high-quality 2D/3D heterostructures for Sn halide PSCs.

4.2.3 | Seed Crystal Engineering for Phase Distribution Control

Seed crystal engineering controls crystallization and phase distribution, mitigating issues from uncontrolled low- n 2D

phases and Sn^{2+} oxidation. Introducing pre-synthesized 2D perovskite microcrystals, such as 3AMPY SnI_4 (3AMPY = 3-(aminomethyl)pyridinium), into precursors ensures uniform 3D phase growth while minimizing low- n ($n \leq 2$) 2D phases [67]. Strong electrostatic and hydrogen bonding between 3AMPY²⁺ and 3D components (Figure 12E), facilitated by nucleation sites, reduces low- n phase signals (via transient absorption spectroscopy) and trap density from 5.79×10^{16} to $4.74 \times 10^{16} \text{ cm}^{-3}$. This extends carrier lifetime from 407.13 to 861.72 ps, increases V_{oc}

from 0.78 to 0.938 V, and boosts PCE from 10.91% to 13.28%, with 96% PCE retention after 3000 h in nitrogen [67]. By inhibiting Sn^{2+} oxidation (Sn^{4+} reduced from 28.5% to 8.4%), this approach aligns material engineering with processing control, enhancing V_{oc} by optimizing phase purity and reducing defects.

4.2.4 | Bulk Defect Suppression Strategies

Managing intrinsic bulk defects within the perovskite lattice, beyond surface passivation, is essential for enhancing V_{oc} . Incorporating large organic cations like piperazine (PZ^{2+}) into FASnI_3 leads to $\text{FA}_{1-2y}\text{PZ}_{2y}\text{Sn}_{1-y}\text{I}_3$ ($0 \leq y \leq 0.25$), preserving 3D continuity without reducing dimensionality [68]. The strong interactions of PZ^{2+} with $[\text{SnI}_6]$ octahedra increase V_{Sn} formation energy, thereby decreasing p-type self-doping and trap states (Figure 12F,G). This results in a three-fold increase in carrier lifetime (from 2.18 to 7.03 ns), a reduction in trap density from 3.46×10^{15} to $1.99 \times 10^{15} \text{ cm}^{-3}$, and a PCE of 9.15%, with over 95% efficiency retention after 1000 h in nitrogen [68]. Enhanced crystallinity and reduced background carrier density further minimize V_{loss} and FF loss resulting from intrinsic defects, complementing surface passivation techniques.

4.3 | Molecular Coordination Approaches

The V_{oc} and FF in Sn halide PSCs are frequently limited by non-radiative recombination and defect states arising from the facile oxidation of Sn^{2+} to Sn^{4+} and uncontrolled crystallization dynamics. Molecular coordination approaches have demonstrated efficacy in overcoming these challenges by leveraging Lewis acid–base interactions to regulate crystallization kinetics, passivate inherent defects, and Sn^{2+} oxidation state [69]. These approaches typically involve the incorporation of molecular additives that coordinate with Sn halide precursors, leading to improved film morphology, suppressed trap-assisted recombination, and enhanced V_{oc} and FF of the device. This section reviews recent advancements in molecular additive engineering, highlighting several multifunctional additives reported in cutting-edge studies. These molecular additives play a crucial role in passivating defects within perovskite materials, thereby significantly reducing non-radiative recombination and minimizing V_{loss} (Table 1). Consequently, the strategic use of these additives has become a powerful approach for enhancing device performance and stability in PSCs.

In FASnI_3 PSCs, hydroxybenzene sulfonic acid derivatives (e.g., KHQSA) with excess SnCl_2 improve performance by forming SnCl_2 additive complexes via SO_3^- coordination with Sn^{2+} , encapsulating grains. The hydroxybenzene group scavenges O_2 , suppressing Sn^{4+} formation. This strategy boosts PCE from 3.53% to 6.76%, with unencapsulated devices retaining 80% efficiency after 500 h in air [70]. Introducing *n*-butylammonium acetate (BAAC) into FASnI_3 promotes $\text{O} \cdots \text{Sn}$ and $\text{N}-\text{H} \cdots \text{X}$ bonding (Figure 13A,B), stabilizing Sn^{2+} against oxidation by DMSO and delaying crystallization. XPS reveals a decrease in $\text{Sn}^{4+}/\text{Sn}^{2+}$ ratio from 18.3% to 6%, enhancing V_{oc} from 0.60 to 0.65 V and improving PCE by 10.4% [71]. Thiosemicarbazide (TSC) passivates CsSnI_3 by coordinating Sn^{2+} via its $\text{S}=\text{C}-\text{N}$ group, increasing Sn vacancy formation energy (1.61–1.74 eV),

thus reducing trap density (1.25×10^{16} to $7.31 \times 10^{15} \text{ cm}^{-3}$), extending PL lifetime (28.0–139.2 ns), and enhancing V_{oc} (0.47–0.63 V). This yields 8.20% PCE with >90% stability after 500 h illumination [72]. Templated growth using SCN and phenylethylamine hydroiodate (phenylethylammonium iodide [PEAI]) in inorganic $\text{CsSnBrI}_{2-x}(\text{SCN})_{2x}$ PSCs promotes a mixed 2D/3D structure, where SCN facilitates a 2D template, leading to out-of-plane orientation and large grain size, reducing defect density to $1.16 \times 10^{16} \text{ cm}^{-3}$. The 2D intermediate ($\text{PEA}_2\text{SnI}_{4-x}\text{SCN}_x$) guides 3D growth, enhancing carrier lifetime and V_{oc} to 0.43 V [73]. This method underscores the additive's role in controlling crystallization kinetics, reducing defects, and improving V_{oc} . Zhong et al. incorporated guanidine thiocyanate (GASCN) into $\text{PEA}_{0.1}\text{FA}_{0.9}\text{SnI}_3$ PSCs, facilitating coordination of SCN^- and guanidinium groups with Sn^{2+} during solution processing. This interaction enables controlled crystallization, effectively decreasing trap density and suppressing Sn^{2+} oxidation to Sn^{4+} . The study suggests that the GASCN additive could help in reducing the band energy level difference, further improving hole mobility (Figure 13C). Consequently, it suppresses interfacial recombinations and promotes the device V_{oc} enhancement [74]. The coordination between Sn^{2+} ions and the sulfur ($\text{S}=\text{C}$) and amine ($-\text{NH}_2$) functional groups in trimethylthiourea (3T) modulates crystallization kinetics, resulting in dense, uniform, and pinhole-free perovskite films. This molecular interaction significantly elevates the V_{oc} from 0.65 to 0.92 V and reduces the V_{oc} deficit (~ 0.2 V) [75]. 2-(2-Aminoethyl)-2-thiopseudourea dihydrobromide (AET) and 2-pyridylthiourea (2PTU), containing $-\text{NH}_2$, $=\text{NH}$, and $-\text{S}-\text{C}$ functional groups, form strong coordination bonds with Sn^{2+} and hydrogen bonds with I^- or Br^- . These interactions promote the formation of stable Lewis acid–base adducts, effectively regulating crystal growth kinetics and enhancing film morphology. As a result, deep-level defects and Sn^{2+} oxidation are significantly suppressed, contributing to improved optoelectronic quality of the perovskite film [76, 77]. Wang et al. used 5-mercapto-1-methyltetrazole tin salt (SnT_2) in FASnI_3 PSCs, where $-\text{S}$ and $-\text{N}$ electron-donating groups coordinate with Sn^{2+} at GBs, tuning energy levels (VB from -5.26 to -5.37 eV, CB from -3.9 to -3.97 eV) (Figure 13D). The trap density decreases from 4.33×10^{15} to $1.93 \times 10^{15} \text{ cm}^{-3}$ (Table 1), and V_{oc} rises to 0.843 V (Figure 13E), indicating suppressed non-radiative recombination loss [6]. Thiophene-2-ethylammonium halides (TEAX, $\text{X} = \text{I}, \text{Br}, \text{Cl}$) maintain the 3D structure while enhancing crystallization, where the sulfur lone pairs coordinate with Sn^{2+} (Figure 13F), reducing Sn^{4+} content, suppressing deep defects, and elevating V_{oc} from 0.42 to 0.56 V (C_{60} contacts) and up to 0.8 V (Indene- C_{60} bisadduct; ICBA contacts) with a PCE of 12% [78]. With $\text{S}=\text{C}-\text{N}$, $-\text{NH}_2$, and a π -conjugated phenyl ring, 4-phenylthiosemicarbazide (4PTSC) forms a $\text{Sn} \cdots \text{S}=\text{C}-\text{N}$ adduct with SnI_2 (Figure 13G), slowing crystallization to yield pinhole-free films with preferred grain orientation. The S-donor and $-\text{NH}_2$ groups passivate uncoordinated Sn^{2+} and halide ions, reducing $\text{Sn}^{4+}/\text{Sn}^{2+}$, boosting V_{oc} from 0.78 to 0.94 V, and achieving a record efficiency of 12.22% (certified 11.70%) [79]. Ren et al. used $\text{Pb}(\text{SCN})_2$ and acetaminophen (ACE) for interfacial coordination in lead-lean Sn-PSCs ($\text{FA}_{0.9}\text{PEA}_{0.1}\text{SnI}_3$ with minor $\text{Pb}(\text{SCN})_2$). ACE's phenolic hydroxyl, acetamino, and $\text{C}=\text{O}$ groups coordinate with Sn^{2+} and I^- at the PEDOT:PSS/perovskite interface, reducing Sn^{2+} oxidation (Figure 13H,I) and trap density (8.62×10^{15} to $5.84 \times 10^{15} \text{ cm}^{-3}$), lifting V_{oc} from 0.55 to 0.70 V [80]. The sulfoxide ($\text{O}=\text{S}=\text{O}$) and bromine groups in BrDS chemically

TABLE 1 | Comparative analysis of molecular additive-induced defect passivation and V_{oc} improvement in Sn halide perovskite solar cells (PSCs).

Molecular additive								
Perovskite	E_g eV	Molecule	Coordination	Defect density	Efficiency	V_{oc}	FF	Ref.
FASnI ₃		KHQSA	Sn...SO ₃ ⁻		6.76	0.55	69	[70]
FASnI ₃		BAAc	Sn...O and N-H...X		10.4	0.65	71.6	[71]
CsSnI ₃	1.3	TSC	Sn...S=C-N	1.25 × 10 ¹⁶ to 7.31 × 10 ¹⁵ cm ⁻³	8.20	0.63	66.1	[72]
CsSnBrI _{2-x} (SCN) _x		SCN and PEAi						
PEA _{0.1} FA _{0.9} SnI ₃	1.38	GASCN		1.16 × 10 ¹⁶ cm ⁻³ 5.08 × 10 ¹⁶ to 2.60 × 10 ¹⁶ cm ⁻³	5.01 10.06	0.43 0.70	68.7 72	[96] [74]
FASnI ₃	1.4	3T	S=C and -NH		14.0	0.92	75.69	[75]
PEA _{0.15} FA _{0.85} SnI ₂ Br		AET	C-S and -NH with Sn ²⁺	1.52 × 10 ¹⁶ and 9.81 × 10 ¹⁵ cm ⁻³	13.55	0.84	80.2	[76]
FASnI ₃		2PTU	=NH ₂ and C=S with SnI ₆ ⁴⁻	4.48 × 10 ¹⁵ and 3.34 × 10 ¹⁵ cm ⁻³	12.85	0.77	71	[77]
(FA _{0.9} DEA _{0.1}) _{0.98} Cs _{0.02}) _{0.98} EDA _{0.01} SnI ₃	1.4	SnT ₂	-S...Sn and N...Sn	4.33 × 10 ¹⁵ and 1.93 × 10 ¹⁵ cm ⁻³	15.33	0.84	73	[6]
FASnI ₃	1.41	TEAX	Sn...S (thiophene)		12	0.8	58	[78]
PEA _{3.15} FA _{0.75} MA _{0.10} SnI ₂ Br	1.65	4PTSC	Sn...S=C-N -NH ₂ ...I	6.75 × 10 ¹⁰ cm ⁻³	12.22	0.94	77.6	[79]
FA _{0.9} PEA _{0.1} SnI ₃	1.38	Pb(SCN) ₂ and ACE	-S and -NH ₂	8.62 × 10 ¹⁵ to 5.84 × 10 ¹⁵ cm ⁻³	12.04	0.70	77.1	[80]
FASnI ₃	1.4	BrDS	O=S=O		14.98	0.79	79.4	[49]
FA _{0.75} MA _{0.25} SnI _{2.75} Br _{0.25} (10% PEAi)		4A3HA	C=O...Sn ²⁺	7.80 × 10 ¹⁵ to 4.05 × 10 ¹⁶ cm ⁻³	13.43	0.84	71.2	[82]
FASnI ₃		HCOO ⁻	-COO...Sn	2.44 × 10 ¹⁷ to 1.54 × 10 ¹⁷ cm ⁻³	12.11	0.71	74	[83]
PEA _{0.15} FA _{0.85} SnI _{2.85} Br _{0.15}		GAA		1.28 × 10 ¹⁶ to 9.80 × 10 ¹⁵ cm ⁻³	13.7	0.93	75	[84]
PEA _{0.15} FA _{0.75} MA _{0.10} SnI ₂ Br	1.68	carboxylate pseudo-halides D-Fo, vanillin	Sn...Fo (COO-)	1.62 × 10 ¹⁶ to 1.02 × 10 ¹⁶ cm ⁻³	10.69	0.79	78.45	[85]
AVI + MAI + SnI ₂ 2D/3D			Sn...OH and -CO		13.18	1.01	75.3	[86]

(Continues)

TABLE 1 | (Continued)

Molecular additive							
Perovskite	E_g eV	Molecule	Coordination	Defect density	Efficiency	V_{oc}	Ref.
FASnI ₃		HaHc	OH...I		9.18	0.67	[43]
CsSnI _{3-x} Br _x	1.34	DMKO	=NOH	1.76 × 10 ¹⁶ to 1.24 × 10 ¹⁶ cm ⁻³	11.2	0.75	[87]
FASnI ₃		FBZAI			13.85	0.77	[88]
FASnI ₃	1.4	MBI		2.03 × 10 ¹⁶ to 1.60 × 10 ¹⁶ cm ⁻³	12.91	0.77	[89]
CsSnI ₃		CBZ	—NH ₂ and —CO	2.01 × 10 ¹⁶ to 1.54 × 10 ¹⁶ cm ⁻³	11.21	0.73	[90]
FASnI ₃		TMAB			5.32	0.46	[91]
FA _{0.75} MA _{0.25} SnI _{2.75} Br _{0.25}		Melamine	C=N and —NH ₂ with Sn ²⁺	2.58 × 10 ¹⁵ to 1.51 × 10 ¹⁵ cm ⁻³	10.30	0.69	[92]
CsSnI ₃	1.3	Pyrrole	N...Sn	3.16 × 10 ¹⁶ to 4.25 × 10 ¹⁶ cm ⁻³	10.11	0.60	[93]
quasi-2D DEA ₂ FA ₈ Sn ₉ I _{28-x} Cl _x -3D		HMCl and DEACl		6.44 × 10 ¹⁵ to 1.126 × 10 ¹⁵ cm ⁻³	9.47	0.60	[94]
FASnI ₃		Pyridyl-substituted fulleropyrrolidines (PPF) with <i>cis</i> -PPF and <i>trans</i> -PPF		1.18 × 10 ¹⁶ to 5.89 × 10 ¹⁵ cm ⁻³	15.38	0.85	[7]
FASnI ₃	1.38–1.40	FBZAX, X = I, Br, Cl			14.13	0.79	[95]

Abbreviations: 4A3HA, 4-amino-3-hydroxybenzoic acid; AET, 2-(2-aminoethyl)-2-thiopseudourea dihydrobromide; BAAC, *n*-butylammonium acetate; BrDS, 2,8-dibromo-dibenzothiothiophene-S,S-dioxide; FBZAI, 4-4-fluorobenzylammonium iodide; FF, fill factor; GASCN, guanidine thiocyanate; PEAI, phenylethylammonium iodide.

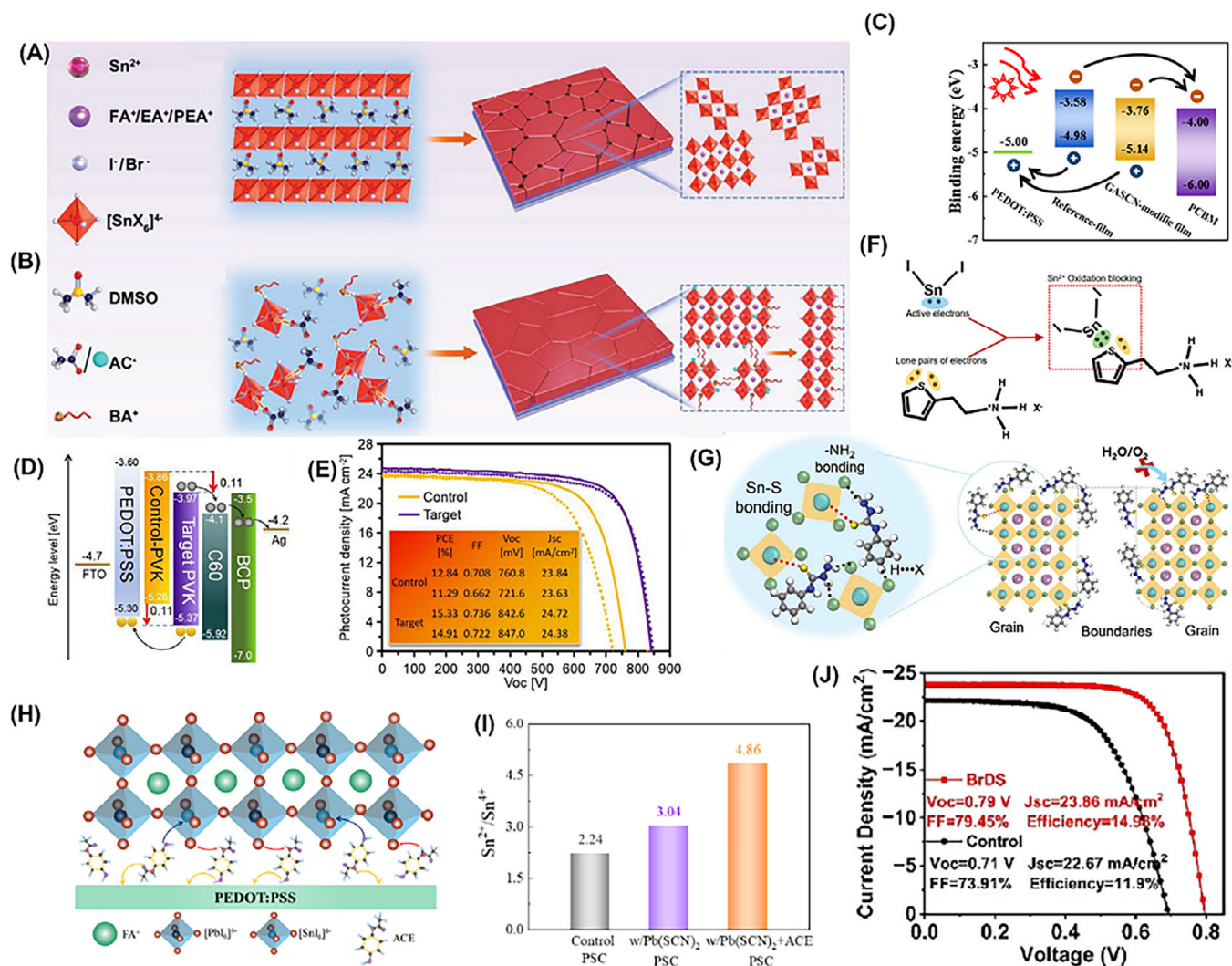


FIGURE 13 | Graphical illustration of BAAC-assisted crystal growth regulation in Sn halide perovskite films: comparison of films processed (A) without and (B) with BAAC. (C) Schematic illustration of the band energy diagram of the Reference perovskite film and GASCN-modified perovskite film. (D) Energy band alignments and (E) current–voltage (*J*–*V*) characteristic curves of Sn PSCs without and with SnT₂ addition. (F) Molecular coordination representation of SnI₂ with TEAX additive. (G) Representation of chemical interaction between the 4PTSC additive and Sn perovskite octahedra and possible defect passivation. (H and I) Graphic scheme of the chemical interaction between ACE/PEDOT:PSS/perovskite and suppression of Sn²⁺ oxidation. (J) *J*–*V* characteristic curve of the control and BrDS-doped PSCs. PSC, perovskite solar cells. *Source*: (A and B) CC BY license [71]. Copyright 2021, John Wiley and Sons. (C) Reproduced with permission [74]. Copyright 2022, John Wiley and Sons. (D and E) Reproduced with permission [6]. Copyright 2024, American Chemical Society. (F) CC-BY 4.0 [78] Copyright 2024, American Chemical Society. (G) CC-BY-NC-ND [79]. Copyright 2024, John Wiley and Sons. (H and I) Reproduced with permission [80]. Copyright 2024, American Chemical Society. (J) Reproduced with permission [49]. Copyright 2024, John Wiley and Sons.

interact with the uncoordinated Sn²⁺, reducing Sn⁴⁺ content and trap density. The device thus delivered over 14% PCE (Figure 13J) with an improved *V*_{oc} of 0.79 V [49].

Li et al. [81] report that a symmetric, nonpolar sulfur-containing ligand, 1,3,5-trithiane (TT), coordinates multisite with Sn²⁺ ions, promoting the formation of large, stable colloidal clusters within the precursor solution. This coordinated clustering, combined with the nonpolar character of TT, facilitates homogeneous nucleation and retards crystal growth, resulting in grains that are both larger and more uniform. Quantitative analysis revealed a significant decrease in hole trap densities from $2.62 \times 10^{15} \text{ cm}^{-3}$ in the control sample to $1.74 \times 10^{15} \text{ cm}^{-3}$ in the TT-based film, alongside a reduction in electron trap densities from 1.57×10^{16}

to $1.13 \times 10^{16} \text{ cm}^{-3}$. Mechanistically, the symmetric sulfur coordination by TT stabilizes Sn²⁺ ions and enforces uniform crystallization, thereby diminishing trap-assisted recombination and enhancing charge extraction efficiency.

Studies indicate that incorporating 4-amino-3-hydroxybenzoic acid (4A3HA) enhances the formation energy of *V*_{Sn} and suppresses Sn²⁺ oxidation by coordinating Sn²⁺ via its carbonyl (C=O) functional group [82]. This effectively reduces Sn⁴⁺ content, elevating the *V*_{oc} from 0.61 to 0.84 V and achieving a PCE of 13.43%. The C=O group in formate (HCOO⁻) strongly coordinates Sn²⁺ in FASnI₃, reducing trap density (2.44×10^{17} to $1.54 \times 10^{17} \text{ cm}^{-3}$), enhancing PL lifetime (1.09–2.83 ns), and increasing *V*_{oc} (0.42–0.71 V), thus demonstrating strong electron-

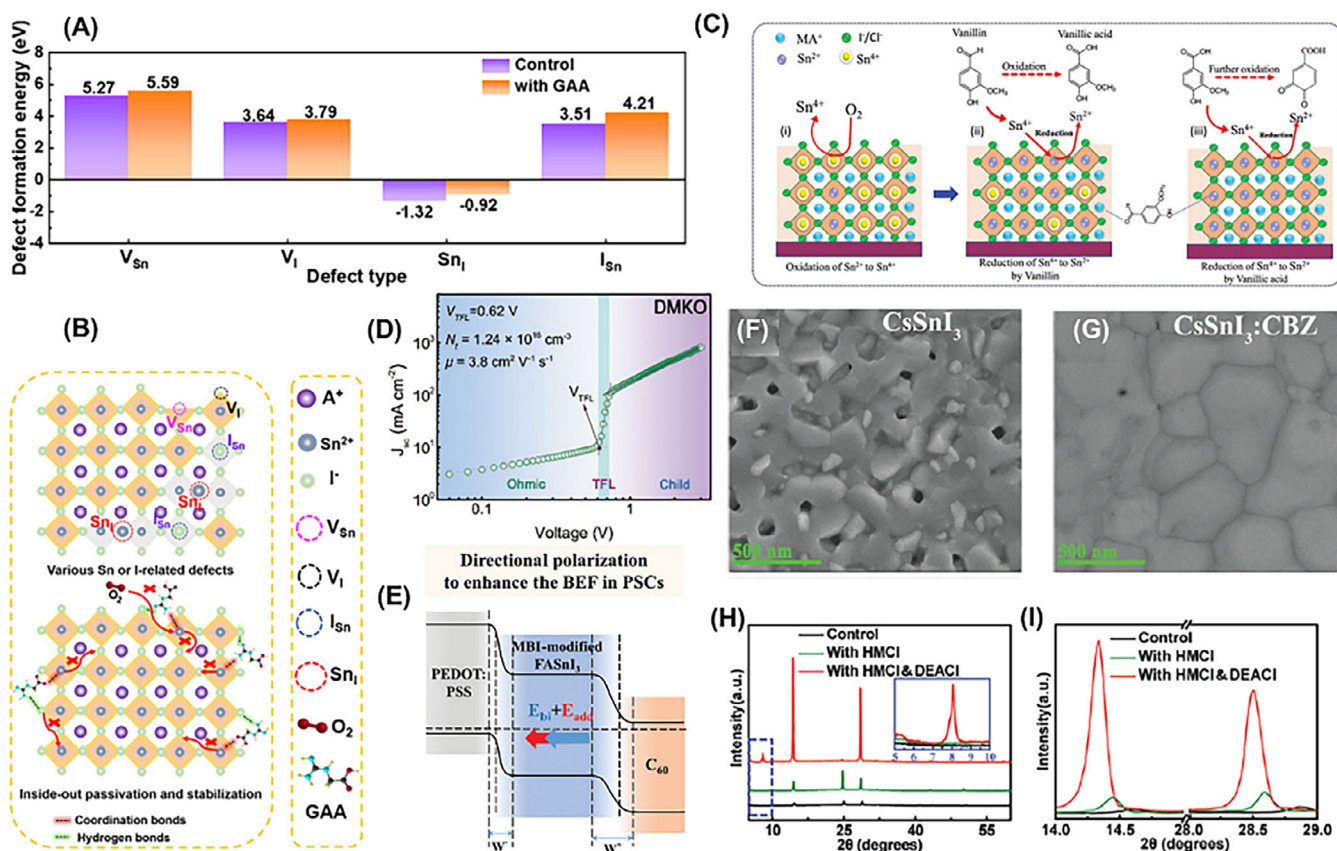


FIGURE 14 | (A) Comparison of formation energies of various defects for control and GAA-modified Sn halide perovskite. (B) Schematic illustration of various defects in the bulk of the Sn perovskite and passivated defect sites in the crystal lattice in GAA-modified perovskite. (C) Graphically represent the two-step redox reaction between vanillin and Sn halide perovskite. (D) Trap density calculation in DMKO-assisted perovskite, through dark $J-V$ curves for the electron-only devices. (E) Energy-level alignment for the inverted MBI-modified Sn PSC. Scanning electron microscopy images of (F) CsSnI $_3$ and (G) CBZ-assisted CsSnI $_3$ perovskite films. (H and I) Comparative x-ray diffraction analysis of control and perovskite films with HMCI and HMCI and DEACI additives. DMKO, Dimethyl ketoxime. *Source:* (A and B) Reproduced with permission [84]. Copyright 2022, John Wiley and Sons. (C) Reproduced with permission [86]. Copyright 2024, John Wiley and Sons. (D) Reproduced with permission [87]. Copyright 2022, John Wiley and Sons. (E) Reproduced with permission [89]. Copyright 2023, John Wiley and Sons. (F and G) Reproduced with permission [90]. Copyright 2023, John Wiley and Sons. (H and I) Reproduced with permission [94]. Copyright 2022, Royal Society of Chemistry.

donating behavior of C=O molecular additives and effective suppression of non-radiative losses [83]. Among various defects, the prominent defect in Sn halide perovskites is the antisite (Sn_I) and vacancy defects (V_{Sn} and V_I) as depicted in Figure 14A, and the defect formation energies of various defects. Liu et al. employed 2-guanidinoacetic acid (GAA) in $PEA_{0.15}FA_{0.85}SnI_{2.85}Br_{0.15}$ PSCs, where the $-NH_2$ and C=O groups coordinate with Sn^{2+} and antisite Sn defect (Figure 14B), further mitigating lattice strain [84]. Cho et al. introduced diphenylamine formate (D-Fo) in $FASnI_{3-x}Br_x$ PSCs, where the C=O (Fo^-) coordinates with Sn^{2+} , reducing Sn^{4+} and trap density from 1.62×10^{16} to 1.02×10^{16} cm $^{-3}$, whereas diphenylamine (DPA^+) enhances stability. The DFT confirms the antioxidant behavior of Fo^- molecule, with adsorption energy (E_{ads}) of -0.52 eV, thus reducing the non-radiative recombinations and V_{loss} [85]. Balilonda et al. introduced vanillin into 2D/3D hybrid Sn perovskites for flexible PSCs. Hydroxyl benzene, ether, and aldehyde groups coordinate with Sn^{2+} and suppress oxidation and deep defect states (Figure 14C). The idea of adding vanillin, lifting V_{oc} from 0.93 to 1.01 V, reached a PCE of 13.18%, the highest for flexible Sn-PSCs [86].

Dong et al. [37] employed hydrazine-acetate (HAAc) to decouple nucleation and growth processes within a DMSO-free, one-step self-assembly method. Acting as a molecular modulator, HAAc stabilizes the precursor chemistry and incorporates HAX species into the lattice in a controlled manner, thereby altering nucleation kinetics. This approach yields compact, uniformly dispersed crystals exhibiting a substantially reduced trap density of 9.85×10^{15} cm $^{-3}$ in the HAAc-modified Sn halide perovskite, compared to 2.92×10^{17} cm $^{-3}$ observed in the $FASnI_3$ control sample.

Hydrogen bonding also plays a crucial role in controlling the defect formation in Sn perovskites. Using HaHc as a molecular additive in $FASnI_3$ is reported to form hydrogen bonds with I^- , whereas Cl^- coordinates with Sn^{2+} , reducing trap density and V_{loss} [43]. Dimethyl ketoxime (DMKO) serves as an effective reductant, scavenging oxygen and converting Sn^{4+} back to Sn^{2+} . Its electron-rich oxime group coordinates Sn^{2+} , passivating Sn interstitials and iodide vacancies. This dual functionality enhances film quality, reduces trap density (1.24×10^{16} cm $^{-3}$), and

minimizes trap-assisted recombination, thereby increasing V_{oc} (Figure 14D). Additionally, DMKO's surface distribution offers in situ device encapsulation [87]. Zou et al. incorporated 4-4-fluorobenzylammonium iodide (FBZAI) into $FASnI_3$ precursors, where benzylamine and fluorine enhance crystallinity and passivate defects, reducing the Sn^{4+} ratio [88]. Introduction of 2-methylbenzimidazole (MBI) delivers $-NH-$ and $=N-$ groups coordinated with Sn^{2+} , reducing trap density to $1.60 \times 10^{16} \text{ cm}^{-3}$. Its ferroelectric polarization enhances (Figure 14E) carrier lifetime and lifts V_{oc} 0.772 V and PCE to 12.91%, with >94% retention after 1056 h in N_2 [89]. The $-NH_2$ and carbonyl ($-CO$) functional groups in carbazide (CBZ) coordinate chemically with Sn^{2+} ions, forming stable acid–base adducts that modulate crystallization kinetics. This controlled crystallization significantly decreases the density of electronic trap states (Figure 14F,G), thereby reducing V_{loss} and highlighting the efficacy of CBZ in defect passivation [90]. Mishra et al. employed trimethylamine borane (TMAB) in combination with SnF_2 for $FASnI_3$ PSCs. The trimethylamine moiety coordinates with Sn^{2+} , modulating crystallization kinetics and suppressing Sn^{2+} oxidation. Simultaneously, the borane component effectively passivates interfacial defects in the NiO HTL, contributing to enhanced film quality and device performance [91]. The $C=N$ and $-NH_2$ functional groups in melamine chemically coordinate with Sn^{2+} in the perovskite precursor, effectively modulating crystallization kinetics. This coordination delays nucleation, resulting in larger grain sizes and lower defect densities. The reduced non-radiative recombination enhances charge carrier dynamics, leading to an improved V_{oc} of 0.69 V [92]. The N-donor sites in pyrrole coordinate with undercoordinated Sn^{2+} , shifting defect levels from 0.674 to 0.218 eV and reducing trap density from 3.16×10^{17} to $4.25 \times 10^{16} \text{ cm}^{-3}$, and suppressing V_{loss} [93]. Another strategy uses hydrochlorides like hydrazine monohydrochloride (HMCl) and diethylamine hydrochloride (DEACl) to form quasi-2D structures (Figure 14H,I). HMCl suppresses Sn^{2+} oxidation, whereas DEACl introduces DEA^+ cations to form $DEA_2FA_8Sn_9I_{28-x}Cl_x$, enhancing morphology and carrier transport in $FASnI_3$. This synergistic approach reduces trap density from 6.44×10^{15} to $1.126 \times 10^{15} \text{ cm}^{-3}$, increases carrier mobility from 1.2524×10^{-4} to $4.4581 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and achieves a PCE of 9.47% with a V_{oc} of 0.601 V. The hydrophobic DEA^+ enhances stability. The V_{oc} increase is attributed to suppressed non-radiative recombination, as shown by a reduced slope in light intensity-dependent V_{oc} measurements ($1.23 \text{ kT}/q$ vs. $1.75 \text{ kT}/q$ for the control) [94]. Studies suggest that the trans-pyridyl groups in trans-pyridyl-substituted fulleropyrrolidine (TPPF) coordinate with Sn^{2+} and control crystal growth kinetics, thus slowing the crystallization by linking perovskite colloids and forming compact films with oriented grains. TPPF at GBs aligns energy levels and suppresses Sn^{4+} formation, further reducing deep defects and lifting V_{oc} from 0.723 to 0.825 V [7]. Jin et al. used 4-fluorobenzylammonium halides (FBZAX) to modulate lattice strain and improve $FASnI_3$ film quality. FBZABr forms Lewis acid–base adducts via its $-NH_3^+$ group, effectively passivating defects and reducing trap density. This enhances crystallinity and suppresses non-radiative recombination, increasing V_{oc} from 0.70 to 0.79 V and achieving a PCE of 14.1% [95].

These studies demonstrate a broad range of coordination strategies for enhancing Sn halide PSCs. Bulk additives, such as 4PTSC [79], TEAX [78], 2PTU [77], melamine [92], HaHc [43], vanillin [86], 4A3HA [82], AET [76], BAAC [71], GAA [84], GASCN [74], 3T

[75], CBZ [90], and D-Fo [85], effectively regulate crystallization kinetics and stabilize Sn^{2+} against oxidation. Interfacial modifiers like thiophenemethylammonium iodides (ThMAI) [73], FBZAI [95], TSC [72], TPPF [7], and SnT_2 [6], along with grain-encapsulating complexes, mitigate non-radiative recombination and surface oxidation. Specific additives target distinct mechanisms: pyrrole passivates deep-level traps, FBZAX [88] relieves lattice strain, MBI [89] introduces ferroelectric domains, and BrDS [49] improves grain morphology. GAA, GASCN, 3T, CBZ, D-Fo, and SnT_2 provide comprehensive defect passivation [6, 74, 75, 84, 85, 90]. The presence of electron-donating atoms (S, N, O, Cl, F, Br) enables strong coordination with Sn^{2+} , forming stable Lewis acid–base adducts that suppress defect formation and oxidation pathways. Future efforts could integrate hybrid molecules with multiple functionalities, such as ferroelectricity, HTL passivation, redox activity, and energy level tuning, to holistically address bulk, surface, and interfacial defects, further closing the V_{oc} deficit in Sn halide PSCs.

4.4 | Perovskite Surface Passivation

Surface passivation plays a critical role in enhancing the V_{oc} of Sn halide PSCs by suppressing non-radiative recombination and mitigating surface oxidation defects. Unlike Pb-based analogs, Sn halide perovskites are more prone to $Sn(II)$ oxidation, leading to deep trap states and greater V_{loss} . Recent progress has focused on chemical surface treatments to improve crystallinity, reduce trap density, and enhance charge transport. This section highlights three effective strategies—chemo-thermal dedoping, fluorinated molecular passivation, and surface recrystallization—demonstrating their impact on V_{oc} improvement through targeted surface engineering. An effective strategy for improving Sn halide perovskite performance involves chemo-thermal surface dedoping, as demonstrated by Zhou et al. [97]. This method targets $Sn(IV)$ self-dopants that predominantly accumulate at the surface of films such as $FA_{0.75}MA_{0.25}SnI_3$. A thin formamidinium chloride (FACl) layer, thermally evaporated and subsequently annealed, reacts with surface $Sn(IV)$ to form a volatile $SnI_4 \cdot xFACl$ complex, which is eliminated during processing (Figure 15A). This treatment preserves bulk morphology while enhancing surface optoelectronic properties, tripling carrier lifetime (5.3–13.4 ns) and halving trap density from 1.05×10^{17} to $4.16 \times 10^{16} \text{ cm}^{-3}$ (Figure 15B). As a result, V_{oc} improves from 0.66 to 0.76 V, and PCE reaches 14.7% (Figure 15C). The Mott–Schottky analysis confirms an increase in built-in potential (0.67 vs. 0.58 V), underscoring the dedoping process's effectiveness in reducing recombination and addressing V_{loss} . Molecular passivation using 4-fluorobenzohydrazide (F-BHZ) has proven effective for wide- E_g ($\sim 1.68 \text{ eV}$) Sn halide perovskites [98]. Khadka et al. treated $(FA, MA, PEA)Sn(I, Br)_3$ films with F-BHZ in trifluoroethanol, improving crystallinity and film compactness. The hydrazide and carbonyl groups coordinate with Sn^{2+} , reducing surface Sn^{4+} content (13.34%–9.30%) and extending carrier lifetimes from τ_1 : 3.23–5.44 ns; τ_2 : 7.51–12.27 ns (Figure 15D). This lowers trap-assisted recombination (V_{oc} slope: 1.22 vs. 1.45 kT/q), raising V_{oc} from 0.914 to 1.024 V and PCE to 11.14%. DFT confirms strong O–Sn binding ($\sim 2.33 \text{ \AA}$) without generating in-gap states, supporting effective defect passivation (Figure 15E). An alternative strategy for surface modification involves iso-butylammonium iodide (iso-BAI)-induced recrystallization, as reported by Chan et al. [99].

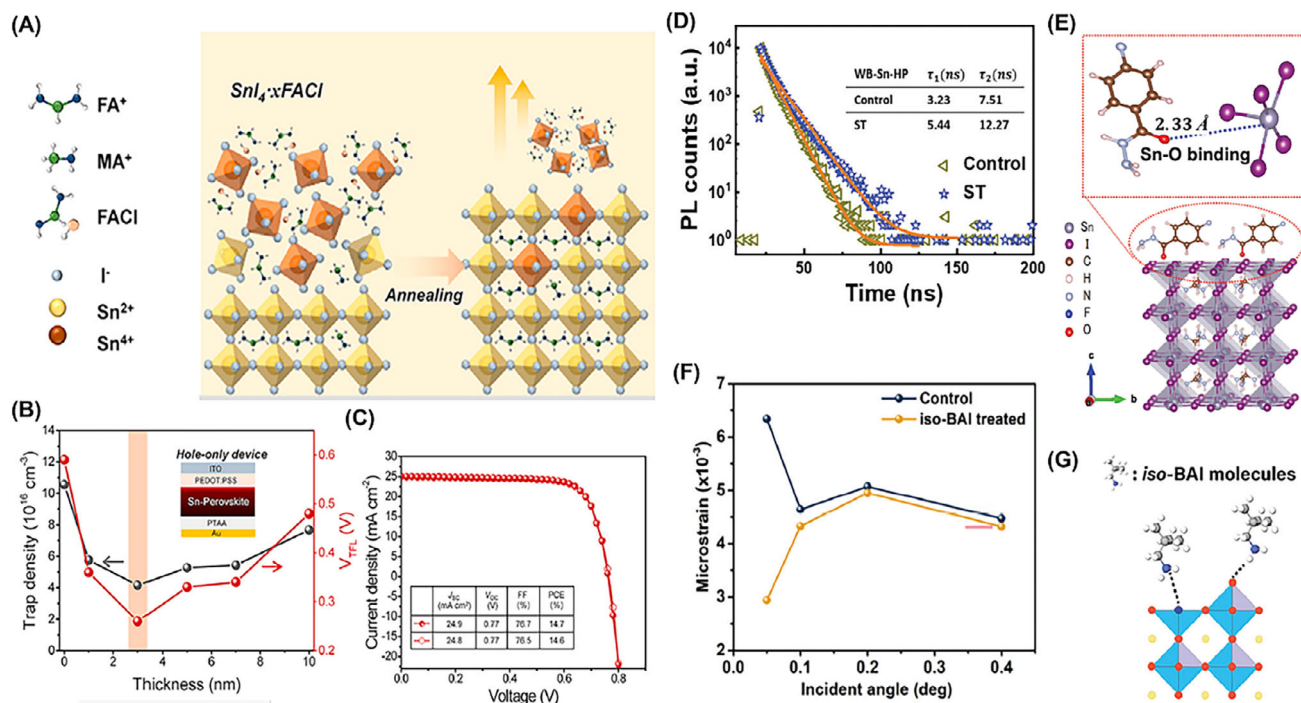


FIGURE 15 | (A) Graphical representation of perovskite surface dedoping via $\text{SnI}_4 \cdot x\text{FACl}$ complex and volatilization. (B) Trap density calculated through space charge limited current measurement of hole-only device of Sn perovskite films with FACl, (C) J - V characteristic curve of champion device. (D) Time-resolved PL decay characteristics of control and F-BHZ-surface-treated Sn halide perovskite, (E) molecular interaction of Sn halide octahedra with F-BHZ molecule through Sn-O bonding. (F) Predicted micro-strain of control and iso-BAI-treated Sn perovskite, (G) schematic representation of chemical interaction between iso-BAI and Sn perovskite. iso-BAI, iso-butylammonium iodide. Source: (A–C) Reproduced with permission [97]. Copyright 2022, Elsevier. (D and E) Reproduced with permission [98]. Copyright 2024, John Wiley and Sons. (F and G) CC BY license [99] Copyright 2024, John Wiley and Sons.

Unlike its conventional role in Pb-based perovskites, where iso-BAI promotes 2D layer formation, Sn halide perovskite drives a surface dissolution recrystallization mechanism in FASnI_3 using a mixed solvent. In situ GIWAXS measurements reveal that iso-BAI facilitates oriented recrystallization, significantly improving surface crystallinity and reducing microstrain (Figure 15F). This process yields pinhole-free films with smoother grains and lowers the $\text{Sn}^{4+}:\text{Sn}^{2+}$ ratio from 0.27 to 0.07. Enhanced surface quality leads to longer carrier lifetimes, improved charge transport, and an increase in V_{oc} from 0.74 to 0.81 V, with a PCE of 14.2%. The Lewis base interaction between iso-BAI and Sn^{2+} further suppresses surface oxidation (Figure 15G), reducing non-radiative losses and enhancing device performance. 2-ThMAI and 3-ThMAI have been employed as surface post-treatments for CsSnI_3 PSC to enhance interfacial properties. The sulfur atom in the thiophene ring coordinates with Sn^{2+} , inducing a favorable interfacial dipole at the $\text{CsSnI}_3/\text{ICBA}$ interface, which effectively eliminates the electron extraction barrier. This modification significantly extends the PL lifetime from 3.94 to 13.56 ns with 3-ThMAI by suppressing non-radiative recombination. As a result, the PCE reaches 12.05% [73].

4.5 | Interfacial Optimization and Passivation Strategies

Interfacial optimization and passivation strategies have emerged as critical approaches to enhance the V_{oc} in Sn halide PSCs by mitigating energy barriers, reducing recombination losses, and

improving charge extraction at key interfaces. The interfaces between the perovskite absorber and CTLs, specifically the HTL and ETL, are pivotal in determining V_{oc} , as they govern carrier dynamics and defect-mediated recombination. In Sn halide PSCs, challenges such as energy level mismatches, Sn(II) oxidation at interfaces, and poor interfacial contact exacerbate V_{oc} deficits. This section reviews recent advancements in interfacial engineering, highlighting innovative substrate modifications, ternary passivation systems, and polymer-doped ETLs to address these issues, significantly boosting V_{oc} and overall device performance.

4.5.1 | Reducing V_{loss} via HTL Interface Engineering

On the hole-transport side, precise alignment between the perovskite VB and the HTL is of paramount importance. One groundbreaking approach involves optimizing the buried interface between the indium tin oxide (ITO) substrate and Sn perovskite by eliminating the HTL, as demonstrated by Liu et al. through a chlorine radical chemical bridging (Cl-RCB) strategy. This method modifies the ITO surface with chlorine radicals generated via UV-ozone treatment in a halogenated solvent (1,2-dichlorobenzene), reducing oxygen vacancies and downshifting the work function from -4.80 to -5.08 eV (Figure 16A,B). This adjustment aligns the ITO's energy level closer to the perovskite's VB, reducing the interfacial energy barrier by 0.20 eV. The Cl-RCB treatment also enhances perovskite crystallinity and shifts residual strain from tensile to compressive at the ITO/perovskite interface. Consequently, trap densities reduced to $3.27 \times 10^{15} \text{ cm}^{-3}$

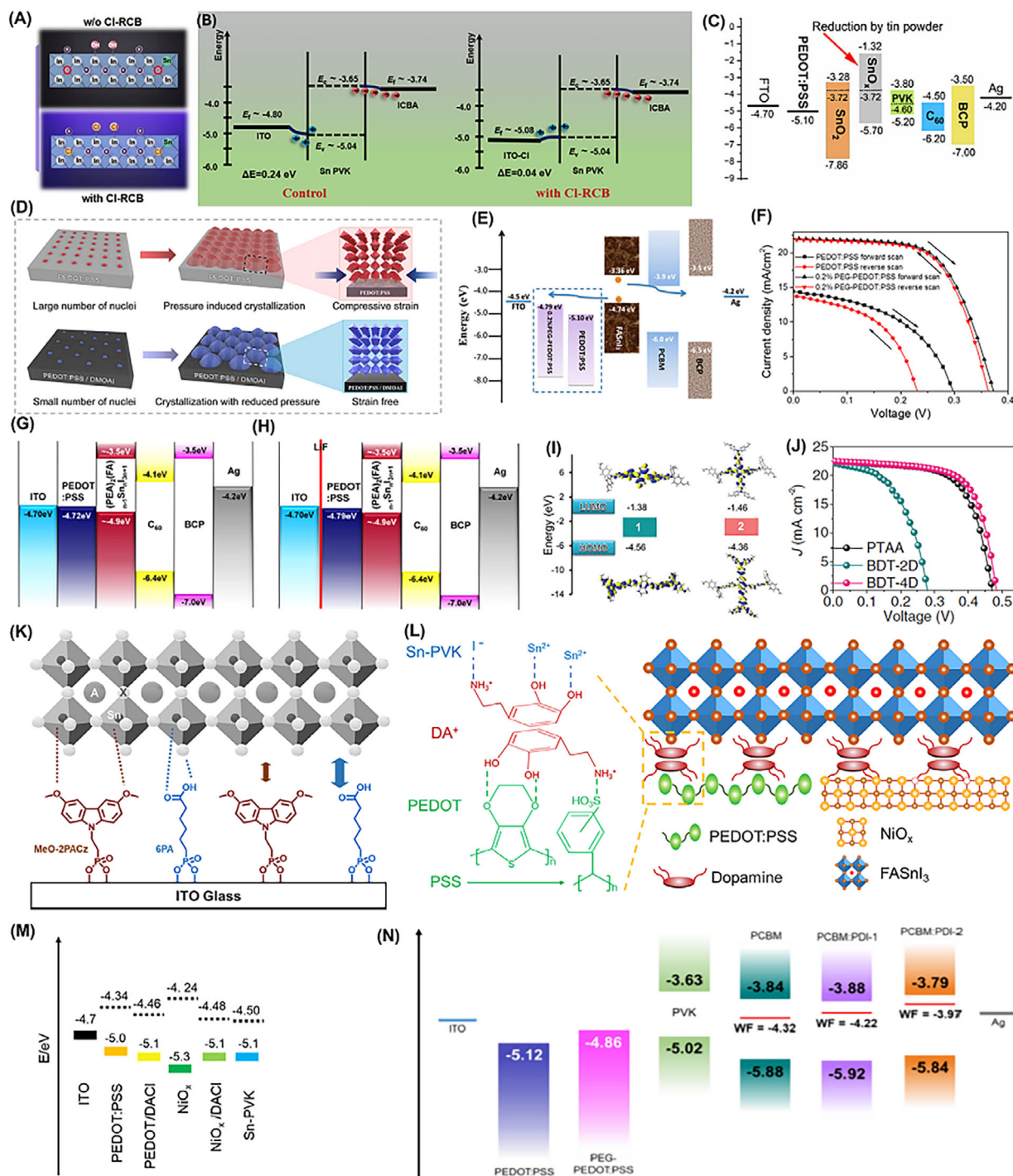


FIGURE 16 | (A) The chlorination process of the ITO upon submersing in halide-comprising reagent under UV–ozone treatment. (B) Energy band alignment representation of the control perovskite and CI-RCB-modified perovskite. (C) Graphic representation of SnO_x and SnO_2 energy levels concerning the Sn halide PSC. (D) Graphical visual of Sn-HP crystal growth mechanisms with reduced surface energy assisted by DMOAI interlayer. (E and F) Energy-level diagram and J–V characteristic curves for Sn PSCs with PEDOT:PSS and PEDOT:PSS/PEG as HTLs. (G and H) Energy band diagram of Sn perovskite without and with ultra-thin LiF layer. (I and J) HOMOs and LUMOs for BDT-2D and BDT-4D molecules derived through DFT study and J–V characteristic curves of PSCs with PTAA, BDT-2D, and BDT-4D HTLs. (K) Graphical representation of chemical interaction between Sn perovskite and MeO-2PACz and 6PA. (L and M) Schematic illustration of the buried HTL/DACI/Sn-perovskite interfaces and energy band alignments. (N) Band energy diagram of the Sn perovskite with specific CTLs in PSCs calculated via UPS measurements. ITO, indium tin oxide. *Source:* (A and B) Reproduced with permission [100]. Copyright 2024, John Wiley and Sons. (C) CC-BY-NC-ND license [102] Copyright 2025, John Wiley and Sons. (D) Reproduced with permission [106]. Copyright 2025, Royal Society of Chemistry. (E and F) Reproduced with permission [108]. Copyright 2018, American Chemical Society. (G and H) Reproduced with permission [109]. Copyright 2018, American Chemical Society. (I and J) Reproduced with permission [110]. Copyright 2019, John Wiley and Sons. (K) Reproduced with permission [111]. Copyright 2024, American Chemical Society. (L and M) Reproduced with permission [112]. Copyright 2025, John Wiley and Sons. (N) Reproduced with permission [113]. Copyright 2024, American Chemical Society.

(Table 2). These improvements led to an HTL-free Sn PSC with a V_{oc} increase from 0.74 to 0.97 V, achieving a PCE of 14.20% [100]. This strategy highlights how substrate-level interfacial passivation can bypass traditional HTL-related recombination losses, significantly enhancing V_{oc} .

A new series of dopant-free pyrrolopyrrole-based (PPr) polymeric HTLs, designed for lead-free TPSCs, was developed using bithiophene derivatives with thioalkylated and alkylated side chains. The PPr-thioalkylated bithiophene (SBT)-14 variant achieved a notable PCE of 7.6%. The enhanced performance is attributed to the highly planar molecular structure, improved π -conjugation, and strong S...S interactions, which facilitate better hole transport and film morphology. The design offers insights into molecular conformations that enhance charge transport and environmental stability in Sn halide PSCs [101]. Solution-processed SnO_x nanocrystal material is used as an HTL to replace the acidic PEDOT:PSS in Sn halide PSCs. Synthesized via a synproportionation reaction between Sn^{4+} and Sn^0 , SnO_x exhibited favorable energy level alignment with FASnI_3 perovskite, improving charge extraction. The introduction of SnO_x led to enhanced crystallinity of the perovskite film and larger grain sizes, contributing to a notable PCE of 11.11%. The study further confirmed the partial reduction of Sn^{4+} and the resulting energy band realignment (Figure 16C), making SnO_x an effective and stable HTL for Sn-PSCs [102]. The integration of nitrogen-doped graphene oxide (N_xGO) into the active layer, HTL, and interface of Sn halide PSCs was shown to enhance both efficiency and stability. The N_xGO inclusion effectively slows down perovskite crystallization, enabling larger grain sizes and thicker, pinhole-free films. Passivate defects and align energy levels for optimal charge extraction. Devices incorporating N_xGO achieved a PCE of 13.26%, with enhanced V_{oc} . Mechanistically, hydrogen bonding and nitrogen functionalities in N_xGO promote chemical interaction with ammonium species in the perovskite precursor, contributing to improved optoelectronic properties and suppressed non-radiative recombination [103].

The interfacial instability and poor morphology in 2D/3D mixed Sn PSCs were addressed by doping hydroxyl-rich d-sorbitol into the PEDOT:PSS HTL. The hydroxyl groups in d-sorbitol form hydrogen bonds with iodide ions in the perovskite, promoting nucleation, enhancing crystallinity, suppressing defect states, and reducing SnI_2 content. The result is smoother, denser perovskite films with better stability and higher performance. The optimized device achieved a PCE of 10.46%, showcasing d-sorbitol as a cost-effective strategy for improved interfacial engineering [104]. Cao et al. demonstrate the enhancement in performance by modifying the buried interface using 2-chloroethylphosphonic acid (CEPA), a halogen-terminated self-assembled monolayer (SAM). CEPA chemically anchors to the PEDOT:PSS layer, reducing excess PSS, suppressing unwanted interfacial reactions, and promoting superior perovskite film morphology. Devices treated with CEPA exhibited a notable PCE increase from 8.57% to 10.65% and improved stability, maintaining performance over 850 h. The CEPA treatment effectively reduces Urbach energy and non-radiative recombination, validating buried interface SAM engineering as a strategic route to boost Sn-PSC efficiency and longevity [105]. Ryu et al. used diethyl-methyl-octadecanoyloxymethyl-ammonium iodide (DMOAI) as

a multifunctional interfacial modifier to regulate crystal growth and reduce defects in Sn halide PSCs. DMOAI modifies the PEDOT:PSS surface and interacts with the perovskite lattice, resulting in improved crystal quality, reduced surface strain (Figure 16D), and enhanced energy level alignment. These effects significantly reduce trap-assisted recombination and increase charge transport efficiency. The resulting device exhibits a PCE of 13.39%, up from 10.42%, and maintains 85% of its initial efficiency after 2500 h in an inert environment. This study confirms DMOAI's effectiveness in addressing key stability and efficiency challenges in Sn-PSCs [106].

Various novel HTLs and interlayers have been explored to this end. For example, Qu et al. introduced a bulky SAM, 2-(7H-dibenzo[c,g]carbazol-7-yl)ethyl phosphonic acid (2PADCB), between PEDOT:PSS and tin (Sn) perovskite layers. This SAM served to passivate the interface and likely adjusted the energy level alignment, thereby enhancing carrier extraction. Devices treated with this SAM achieved a PCE of 14.7%, compared to 12.5% for control samples [107]. The authors attributed these improvements to enhanced interface quality and suppressed recombination, implicitly reflecting improved energy matching. Additional studies have suggested that incorporating Sn-perovskite quantum dots or interlayers at the HTL can establish a cascade VB structure. For instance, cesium-tin perovskite quantum dots deposited atop a 3D formamidinium lead iodide (FAPbI_3) perovskite absorber create a staggered energy ladder that facilitates hole transfer to the HTL, resulting in increased PCE from 22.99% to 25.72% and likely higher V_{oc} [33].

Liu et al. [108] addressed the significant energy-level mismatch between the shallow VB of FASnI_3 (−4.74 eV) and the deeper work function of conventional PEDOT:PSS (−5.10 eV), which contributed to V_{loss} and pronounced hysteresis. By intercalating polyethylene glycol (PEG) into PEDOT:PSS, the HTL's work function was shifted upward to approximately −4.79 eV, substantially reducing the ~0.36 eV mismatch at the perovskite/HTL interface. This improved alignment minimized interfacial barriers and suppressed non-radiative recombination, facilitating more efficient hole extraction. Consequently, devices exhibited significantly enhanced V_{oc} , improved reproducibility, reduced hysteresis, and increased FF, with PCE rising from 2.01% to 5.12% (see Figure 16E,F).

Ran et al. [109] implemented a bilateral interface engineering strategy by incorporating a PEAI layer at the perovskite surface to form a stable 2D/3D bulk heterojunction, alongside deposition of an ultrathin lithium fluoride (LiF) layer at the ITO/PEDOT:PSS interface. The PEAI layer enhanced film surface coverage and inhibited Sn^{2+} oxidation, thereby passivating interfacial traps that contribute to V_{loss} . The LiF interlayer reduced the work function of PEDOT:PSS and promoted more efficient hole extraction at the HTL/electrode interface. Collectively, these modifications diminished non-radiative recombination, improved energy-level alignment, and enhanced carrier selectivity. As a result, devices achieved a V_{oc} of 0.47 V and an FF of 0.74, culminating in a PCE of 6.98%, marking a significant advancement for Sn halide PSCs. The concurrent improvements in V_{oc} and FF were attributed to the synergistic effects of structural passivation and optimized HTL energetics (refer to Figure 16G,H).

TABLE 2 | Comprehensive analysis of interfacial engineering strategies at the perovskite/charge transport layer (CTL) interface for suppressing V_{loss} in Sn halide perovskite solar cells (PSCs).

Perovskite	Bandgap E_g (eV)	Device structure	Defect density	V_{oc} (V)	V_{loss} (V)	J_{sc} mA cm^{-2}	FF (%)	Efficiency (%)	Ref.
HTL									
CsSnI ₃	1.3	Cl-RCB-modified ITO/Sn perovskite/PTAA/Ag	6.53×10^{15} to $3.27 \times 10^{15} \text{ cm}^{-3}$	0.97	0.33	20.02	73	14.20	[100]
FASnI ₃	1.4	ITO/PPr-BT-14/FASnI ₃ /C ₆₀ /BCP/Ag		0.51	0.89	22.37	66.1	7.6	[101]
FASnI ₃	1.4	ITO/SnO _x /Perovskite/C ₆₀ /BBCP/Ag		0.69	0.71	21.46	75	11.11	[102]
FA _{0.8} MA _{0.2} SnI ₃	1.38	FTO/PEDOT:PSS-N _x GO/Al ₂ O ₃ -N _x GO/Sn-PS:N _x GO/PCBM/BCP/Au	$1.14 \times 10^{16} \text{ cm}^{-3}$	0.96	0.42	21.21	65.05	13.26	[103]
PEA _{0.1} (FA _{0.75} MA _{0.25}) _{0.9} SnI ₃	1.33	ITO/intrinsic or d-sorbitol-doped PEDOT:PSS/PEA _{0.1} (FA _{0.75} MA _{0.25}) _{0.9} SnI ₃ /2,2'',7,7''-tetrakis[N,N'-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD))/Au	$4.54 \times 10^{12} \text{ cm}^{-3}$	0.83	0.50	19.24	65.51	10.46	[104]
FA _{0.75} MA _{0.25} SnI ₃	1.34	ITO/PEDOT:PSS/FA _{0.75} MA _{0.25} SnI ₃ /C ₆₀ /BCP/Ag		0.64	0.70	23.17	71.81	10.65	[105]
PEA _{0.10} FA _{0.75} EA _{0.15} SnI _{2.15} Br _{0.85}	1.43	ITO/PEDOT:PSS/DMOAI/Sn-HP/C ₆₀ /BCP/Ag		0.89	0.54	16.00	80.47	11.78	[106]
EDA _{0.01} (GA _{0.06} (FA _{0.8} CS _{0.2}) _{0.94}) _{0.98} SnI ₂ Br	1.62	ITO/PEDOT:PSS/2PADCB/perovskite/C ₆₀ /BCP/Cu		0.84	0.78	23.5	74.8	14.7	[107]
FASnI ₃	1.37	FTO/PEDOT:PSS/0.2%PEG/perovskite/PCBM/BCP/Ag		0.37	1.0	22.06	62.7	5.12	[122]
(PEA) ₂ (FA) _{n-1} Sn _n I _{3,n+1}	1.38	ITO/PEDOT:PSS/(PEA,FA)SnI ₃ /C ₆₀ /BCP/Ag		0.47	0.91	20.07	74.0	6.98	[109]
FASnI ₃	1.50	FTO/TiO ₂ /FASnI ₃ /FASnI ₃ capping/BDT-4D/Au		0.49	1.01	22.41	68.21	7.59	[110]
PEAFASnI ₃	1.40	ITO glass/SAM/tin perovskite/ICBA/BCP/Ag	$8.61 \times 10^{15} \text{ cm}^{-3}$	0.82	0.58	17.6	64.5	9.4	[111]
PEA _{0.15} FA _{0.85} SnI ₃		ITO/HTL/Sn perovskite/ICBA/BCP/Ag		0.87		22.70	71.84	14.18	[112]
FASnI ₃	1.39	ITO/PEDOT:PSS-PEG/Perovskite/PCBM-PDI/Cu	$4.93 \times 10^{15} \text{ cm}^{-3}$	0.71	0.68	24.42	58	10.1	[113]

(Continues)

TABLE 2 | (Continued)

Perovskite	Bandgap E_g (eV)	Device structure	Defect density	V_{oc} (V)	V_{loss} (V)	J_{sc} $mA\ cm^{-2}$	FF (%)	Efficiency (%)	Ref.
ETL									
($CS_{0.02}FA_{0.9}DEA_{0.1}Br_{0.98}I_3$) PEA:FA:SnIBr	1.4	Fluorine-doped tin oxide (FTO)/PEDOT:PSS/Perovskite/PPI/ C_{60} /BBCP/Ag ITO/PEDOT:PSS/Perovskite/PNDI-BT-ICBA/BCP/Ag	$4.05 \times 10^{15}\ cm^{-3}$ $3.8 \times 10^{16}\ cm^{-3}$	0.75 0.80	0.65	25.83 22.28	75.3 77.80	14.64 13.90	[114] [115]
EDA $_{0.01}FA_{0.98}SnI_{2.98}Br_{0.02}$ FASnI $_3$	1.38 1.37	ITO/PEDOT:PSS/Perovskite/ C_{60} /BCP/Cu FTO/TiO $_2$ /ZnSFASnI $_3$ /PTAA/Au		0.80 0.38	0.58 0.90	23.58 23.09	78.85 60.01	14.91 5.27	[116] [117]
FASnI $_3$	1.37	ITO/ETL/FASnI $_3$ /PTAA/Au		0.42	0.95	22.8	52	5.1	[44]
FASnI $_3$		ITO/PEDOT:PSS/FASnI $_3$ /PCBM or PCBM:N2200/BCP/Ag		0.79		22.5	73	12.98	[32]
PEA $_{0.15}FA_{0.85}SnI_3$ PEAFASnI $_3$		ITO/PEDOT:PSS/perovskite/fullerene ETL/BCP/Ag ITO/PEDOT:PSS/perovskite/Multidentate fullerene/PCBM/BCP/Ag		0.90 0.86		21.39 24.54	0.75 71.06	14.58 15.05	[36] [118]
PEA $_{0.15}FA_{0.85}SnI_3$	1.35	ITO/PEDOT:PSS/PPF4-Perovskite/PCBM/BCP/Ag	$3.99 \times 10^{15}\ cm^{-3}$	0.86	0.49	26.17	71.35	16.05	[119]
FA $_{0.75}MA_{0.25}SnI_{2.75}Br_{0.25}$ FASnI $_3$		ITO/PEDOT: PSS/FA $_{0.75}MA_{0.25}SnI_{2.75}Br_{0.25}$ /CF $_3$ PEAI/PCBM/BCP/Ag ITO/PEDOT/perovskite/ICBA/Ag	$3.40 \times 10^{15}\ cm^{-3}$	0.73 0.97				10.35 15.7	[121] [120]

Abbreviations: BDT, benzodithiophene; DMOAI, diethyl-methyl-octadecanoyloxy-methyl-ammonium iodide; ETL, electron transport layer; ITO, indium tin oxide; PEA1, phenylethylammonium iodide; SAM, self-assembled monolayer.

Vegiraju et al. [110] developed novel benzodithiophene (BDT)-based small-molecule HTLs, specifically BDT-2D and BDT-4D, featuring di- and tetra-triphenylamine substituents, as alternatives to conventional doped HTLs. These HTLs exhibited suitable HOMO levels (~ -4.56 and -4.36 eV) that aligned well with the VB of Sn perovskites, ensuring efficient hole extraction with minimal energetic loss. Additionally, these materials provide intrinsic conductivity and stability, thereby avoiding extrinsic recombination pathways. By reducing interfacial trap states and facilitating smoother energy-level matching, devices incorporating these HTLs demonstrated enhanced V_{oc} and FF relative to controls, achieving champion PCEs of 7.59%. Thus, BDT-based HTLs effectively suppressed non-radiative recombination at the perovskite/HTL interface and improved charge selectivity, directly mitigating V_{loss} and enhancing FF (see Figure 16I,J).

Song et al. [111] demonstrated the substitution of PEDOT:PSS with mixed SAMs as HTLs in tin-based PSCs. By combining MeO-2PACz and 6-phosphonohexanoic acid (6PA), the mixed SAM formed a surface exhibiting strong anchoring to ITO and favorable interactions with Sn perovskites, promoting dense nucleation and high-quality perovskite crystallization. The absence of hygroscopic dopants prevented interfacial degradation commonly associated with PEDOT:PSS, thereby reducing trap formation and recombination. Furthermore, the mixed SAM suppressed iodide vacancies through hydrogen bonding and coordination with Sn^{2+} ions, further diminishing non-radiative recombination (see Figure 16K). With optimized perovskite crystallization and improved interfacial energetics, devices achieved a record V_{oc} of 0.829 V and a PCE of 9.4%, demonstrating both reduced V_{loss} and enhanced FF compared to earlier SAM-based HTLs.

Ma et al. [112] introduced dopamine hydrochloride (DACl) as an interfacial modifier to improve the buried perovskite/HTL interface via multifunctional bonding. The $-NH_3^+$ groups of DACl formed hydrogen bonds with iodide anions, while the $-OH$ groups coordinated with Sn^{2+} ions, effectively suppressing oxidation to Sn^{4+} and passivating interfacial defects. Concurrently, DACl interacted with PEDOT:PSS through N-H...S hydrogen bonding and with NiO_x via coordination with nickel species, thereby neutralizing the corrosive effects of PEDOT:PSS and reducing the oxidative Ni^{3+}/Ni^{2+} ratio in NiO_x . UPS measurements revealed that DACl shifted the VBM of PEDOT:PSS from -5.05 to -5.15 eV and that of NiO_x from -5.36 to -5.13 eV, aligning both with the perovskite VBM and lowering the hole-extraction barrier. These combined effects enhanced V_{oc} from 0.77 to 0.87 V with PEDOT:PSS and from 0.74 to 0.83 V with NiO_x , while also increasing the FF from approximately 65.49% to 71.50%. Consequently, PCE improved from 11.15% to 14.18% and from 12.09% to 14.11%, respectively. Therefore, DACl's multiple hydrogen and coordination bonds simultaneously stabilize Sn^{2+} , protect HTLs, and optimize energy-level alignment, directly reducing V_{loss} and enhancing FF (refer to Figure 16L,M).

Molecular doping of both HTL and ETLs to overcome crystallization challenges and energy-level mismatches was explored where PEG was incorporated into PEDOT:PSS (as HTL), and perylene diimide (PDI) derivatives were added to PCBM (as ETL), forming a charge-transfer complex that improves film formation, charge mobility, and energy alignment (Figure 16N). The dual doping

strategy resulted in a PCE of 10.1% for $FASnI_3$ -based PSCs. This approach offers a universal and eco-friendly route to enhance optoelectronic performance in perovskite PVs [113].

4.5.2 | Reducing V_{loss} via ETL Interface Engineering

Another effective interfacial strategy targets the perovskite/ETL interface using a ternary passivation system, as explored by Wang et al. with a blend of PCBM, poly(3-hexylthiophene-2,5-diyl) (P3HT), and ICBA named PPI system. This approach optimizes energy level alignment and carrier transport by leveraging ICBA's LUMO (-3.74 eV) for reduced band offset with the perovskite, PCBM's superior electrical properties, and P3HT's ability to form a well-connected network (Figure 17A,B). Applied post-perovskite deposition, the PPI system enhances electron extraction and an increased built-in potential, supporting a V_{oc} rise from 0.687 to 0.753 V and a PCE of 14.64% [114].

He et al. [115] reported the incorporation of a polymeric n-type semiconductor, PNDI-BT, blended with ICBA as the ETL, which markedly diminished the V_{loss} relative to the use of ICBA alone. This enhancement is attributed to the improved alignment of the CBM of PNDI-BT (-3.71 eV) with that of the tin-based perovskite, thereby minimizing the interfacial energy offset that typically results in energy dissipation. Furthermore, PNDI-BT exhibits substantially higher electron mobility compared to ICBA, facilitating more rapid electron extraction and reducing electron residence time at the perovskite/ETL interface, which in turn suppresses non-radiative recombination. TRPL measurements demonstrated accelerated quenching with the PNDI-BT/ICBA composite, confirming efficient charge extraction. Additionally, the hydrophobic character of the polymer serves to protect the perovskite from moisture-induced Sn^{2+} oxidation, a process that otherwise generates trap states and degrades V_{oc} over time (see Figure 17C-E). This tailored ETL configuration enhanced the PCE to 13.90%, compared to 12.75% with ICBA alone, while also improving ambient stability. Collectively, these effects reduced non-radiative loss pathways and yielded an elevated V_{oc} [115]. The concept of light-induced interface doping (LIID) as a strategy to enhance the performance of Sn halide PSCs was explored in a recent investigation. Under illumination, advantageous ion migration (Figure 17F) and oxidation at the perovskite/ C_{60} interface improve carrier transport and band alignment, thereby increasing V_{oc} and sustaining a high short-circuit current density, culminating in a PCE of 14.91% [116].

Energy-level mismatches at the ETL/Sn-absorber or HTL/Sn-absorber interfaces induce built-in potential losses and promote non-radiative recombination, which collectively diminish V_{oc} . To address this, various ETL engineering approaches have been developed to optimize energy-level alignment and enhance V_{oc} . For instance, Ke et al. [117] introduced a thin ZnS interlayer between TiO_2 and $FASnI_3$, resulting in a TiO_2 -ZnS cascade conduction band structure that smooths the energy offset and suppresses interfacial recombination. This modification yielded an increased V_{oc} of 0.380 V and a PCE of 5.27%, surpassing the performance of devices employing bare TiO_2 (Figure 17G).

Tin-based perovskites inherently exhibit substantial V_{oc} deficits, partly due to their shallower conduction bands, which create

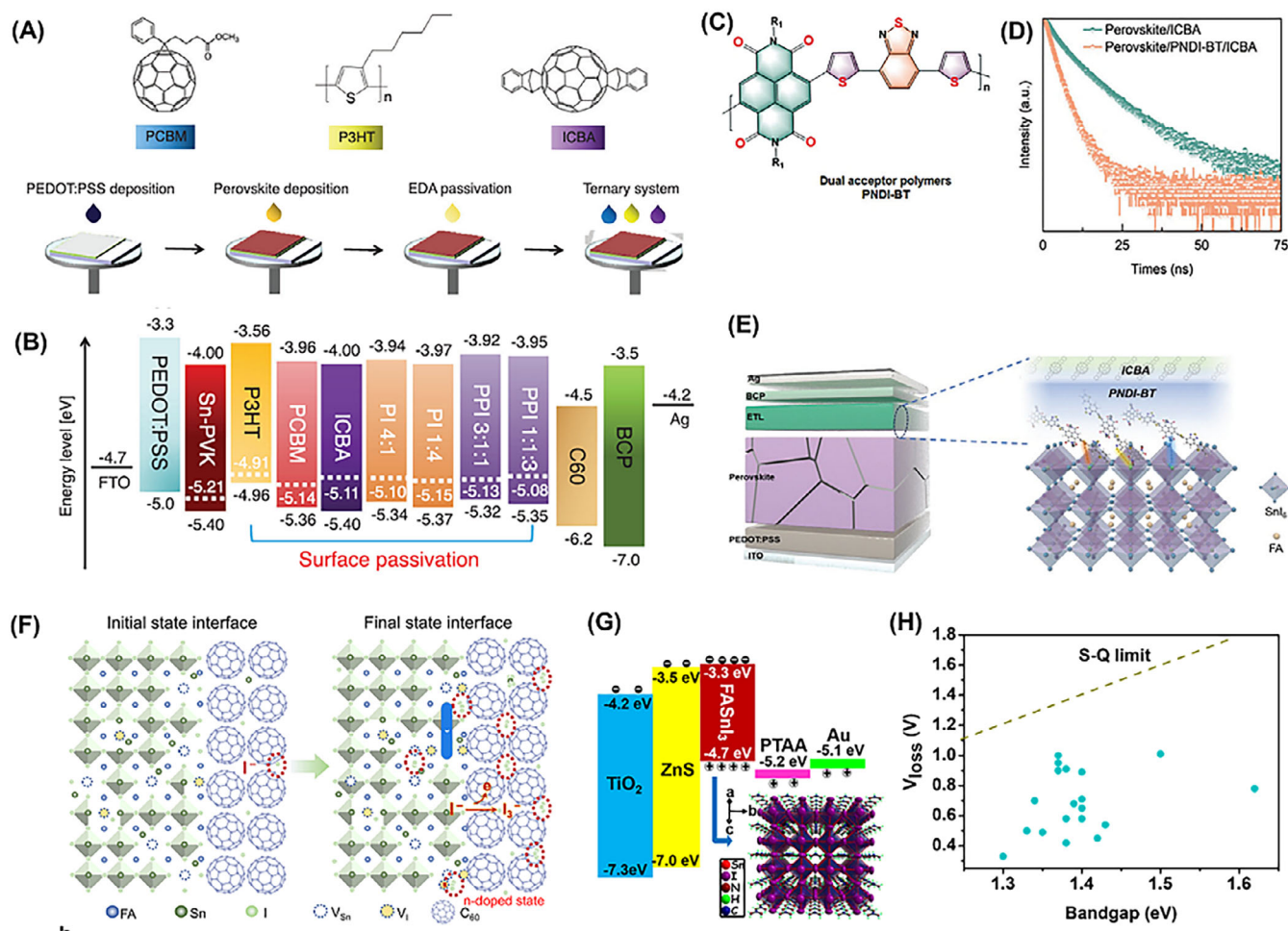


FIGURE 17 | (A and B) Chemical structures of organic materials used as a mixed electron transport layer, corresponding deposition process, and energy band alignment in Sn halide PSC device. (C–E) Illustration of PNDI-BT molecule surface-treated Sn halide PSC with possible molecular interactions. (F) Schematic illustration depicting the alterations in lattice parameters at the perovskite/C₆₀ interface induced by light illumination. (G) Band alignment in FASnI₃ PSC following the incorporation of a ZnS interlayer atop the TiO₂ layer. (H) Voltage loss (V_{loss}) versus bandgap for all Sn halide PSC data represented in Table 2. Source: (A and B) CC-BY-NC license [114] Copyright 2024, John Wiley and Sons. (C–E) Reproduced with permission [115]. Copyright 2024, John Wiley and Sons. (F) Reproduced with permission [116]. Copyright 2025, American Chemical Society. (G) Reproduced with permission [117].

significant offsets with conventional ETLs. Specifically, tin perovskites possess lower electron affinity than their lead counterparts, leading to a pronounced CBO at the interface with TiO₂ ETLs, which contributes to considerable V_{loss} . Yokoyama et al. [44] quantitatively assessed this phenomenon in tin PSCs, demonstrating that precise control of the ETL interface is critical; the use of an Nb₂O₅ ETL, characterized by a near-zero CBO, elevated the V_{oc} beyond that achieved with TiO₂ or SnO₂ ETLs. Another approach involves ETL doping, or the introduction of interlayers to modulate band edge positions. Kayesh et al. [32] doped a C₆₀ derivative ETL (PCBM) with the n-type polymer poly[*N,N'*-bis(2-octyldodecyl)-naphthalene-1,4,5,8-tetracarboximide-2,6-diyl]alt-5,5'-(2,2'-bithiophene) (N2200). This doping raised PCBM's LUMO from -4.00 to -3.83 eV, narrowing the CBO with FASnI₃ from 0.38 to 0.21 eV. N2200's S and O atoms coordinated with Sn(II), suppressing Sn(IV) formation and improving surface stability. As a result, electron mobility, carrier lifetime, and interfacial contact improved, boosting V_{oc} from 0.72 to 0.79 V and achieving a PCE of 12.98% [32]. In summary, ETL doping, or the incorporation of polar

interlayers, can effectively fine-tune band alignment and mitigate V_{loss} by diminishing interfacial energy barriers.

A comprehensive summary of the relationship between V_{loss} and bandgap for all reported Sn halide PSCs incorporating interfacial optimizations is presented in Figure 17H. Corresponding device architecture and performance metrics are detailed in Table 2. Notably, compared to FASnI₃ and (PEA)₂(FA)_{*n*-1}Sn_{*n*}I_{3*n*+1}, CsSnI₃ exhibits relatively lower V_{loss} , approximately 0.3 V. Importantly, V_{oc} demonstrates a strong dependence on both the perovskite bandgap and the interfacial energy alignment at the perovskite/CTL interface.

Sun et al. [36] conducted a systematic isolation of individual regioisomers of a fullerene bisadduct (DCBA) and employed them as ETLs, revealing that the specific isomer selected significantly influenced the V_{oc} . Notably, the trans-3 isomer yielded the highest V_{oc} , attributable to its conduction band edge being positioned at a shallower energy level, thereby achieving closer alignment with the perovskite conduction band. This alignment effectively

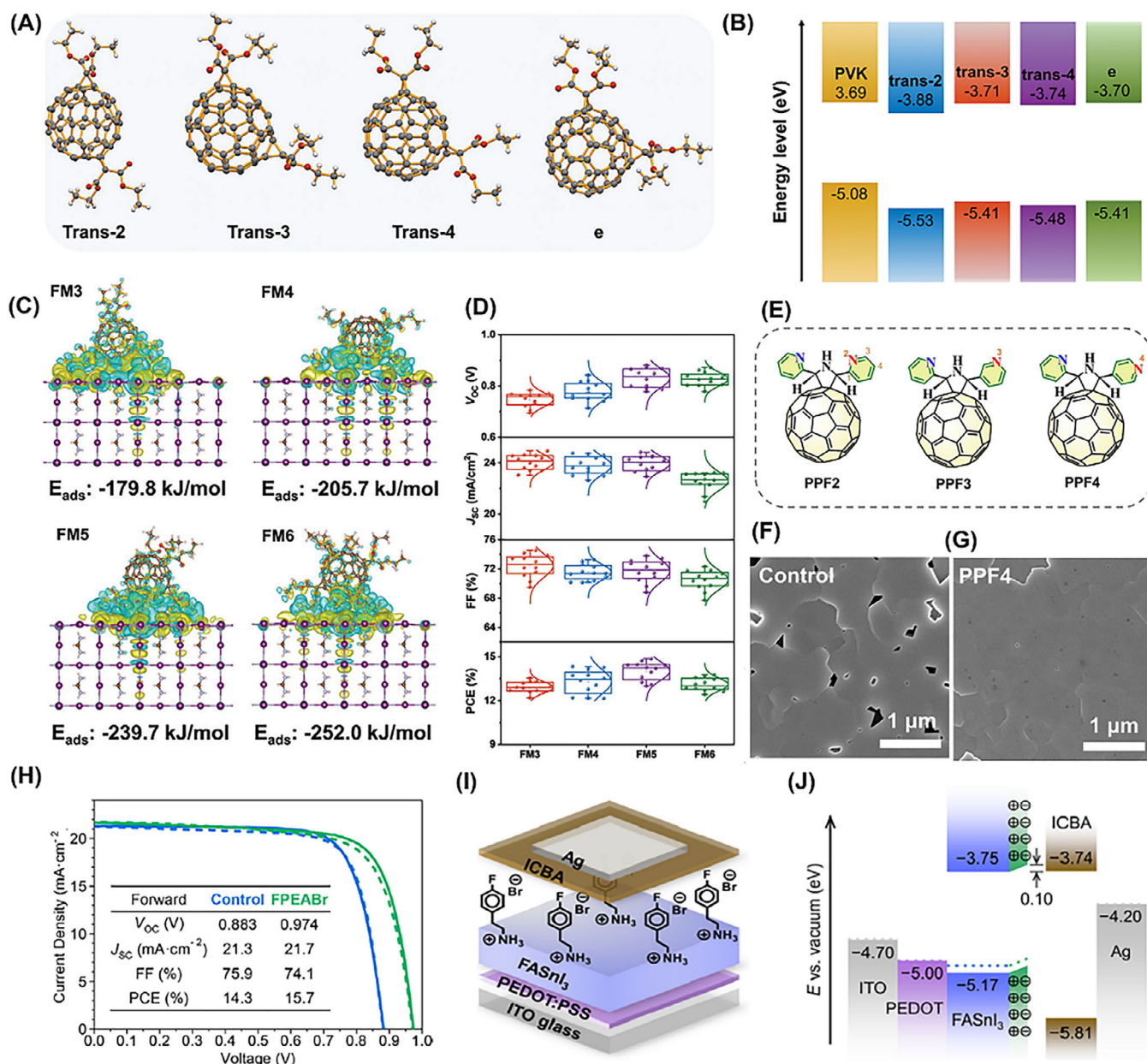


FIGURE 18 | (A) Molecular structures of *trans*-2, *trans*-3, *trans*-4, and regioisomer (B) band energy illustration of the perovskite and fullerene ETLs. (C and D) DFT structural models and absorption energies of PCBM and fullerene derivatives over perovskite, and corresponding *J*-*V* parameters. (E-G) Chemical coordination mechanism between fulleropyrrolidine derivatives and Sn perovskite, SEM images of perovskite without and with PPF4 fulleropyrrolidine. (H-J) *J*-*V* curve of Sn PSC without and with FPEABr treatment, corresponding inverted device structure, and energy band alignment diagram. ITO, indium tin oxide. Source: (A and B) Reproduced with permission [36]. Copyright 2023, John Wiley and Sons. (C and D) Reproduced with permission [118]. Copyright 2024, John Wiley and Sons. (E-G) Reproduced with permission [119]. Copyright 2025, John Wiley and Sons. (H-J) Reproduced with permission [120]. Copyright 2024, American Chemical Society.

mitigated the energy-level mismatch that commonly contributes to V_{loss} (see Figure 18A,B).

In a related investigation, a research group engineered a series of fullerene derivatives (FM3–FM6) functionalized with multiple diethylmalonate groups to serve as multidentate ETLs, with FM5 demonstrating superior performance [118]. The incorporation of additional functional groups induced a shift in the LUMO levels of these fullerene derivatives toward shallower energies, enhancing their alignment with the conduction band of tin-based perovskites and thereby reducing V_{loss} due to energy-level mis-

match. Importantly, the presence of multiple anchoring groups facilitated multivalent bonding between the fullerene molecules and the perovskite surface, establishing a robust and stable interface while passivating undercoordinated tin ions, which are recognized as prominent recombination centers (refer to Figure 18C). FM5 achieved an optimal balance characterized by a sufficiently shallow LUMO, effective passivation, and favorable molecular packing that preserved exposure of the carbon cage, promoting efficient electron transport. This synergy resulted in accelerated electron extraction, as corroborated by PL measurements, and substantially diminished interfacial non-radiative

recombination, as evidenced by enhanced V_{oc} and a PCE of 15.05% (Figure 18D). Furthermore, the strong interfacial bonding and protective molecular arrangement conferred by FM5 contributed to exceptional device stability.

Chen et al. [119] adopted a dual-faceted approach to mitigate V_{loss} in Sn-PSCs by concurrently enhancing the perovskite bulk quality and optimizing the ETL/perovskite interface. Initially, they synthesized pyridyl-substituted fulleropyrrolidines (PPF2-4) as precursor additives; among these, PPF4 was particularly effective in decelerating crystallization and fostering the formation of larger, defect-free grains through its binding affinity to precursor colloids, while also inhibiting the oxidation of Sn^{2+} . This strategy yielded perovskite films with reduced trap densities and diminished bulk non-radiative recombination, thereby directly improving V_{oc} . Subsequently, a bisadduct fullerene ($C_{60}BB$) was introduced as an interfacial layer between the perovskite and the PCBM ETL, which refined the energy-level alignment by decreasing the CBO at the interface. This combined methodology addressed both bulk and interfacial contributors to V_{loss} : PPF4 minimized trap-assisted recombination within the perovskite bulk, and $C_{60}BB$ alleviated the energetic barrier at the ETL interface. The integrated approach culminated in a record V_{oc} and a certified PCE of 15.86%, with a champion device achieving 16.05% (Figure 18E–G). This study compellingly demonstrated that simultaneous mitigation of energy-level mismatch and defect-induced non-radiative recombination is critical for minimizing V_{loss} in Sn halide PSCs.

To address V_{loss} by interface defects and non-radiative recombination, Chen et al. introduce 3-(trifluoromethyl) (CF_3) PEAI for surface passivation. The bulky molecule minimizes trap states, relieves tensile strain, and forms a 2D Sn-perovskite layer that enhances vertical charge transport. Devices treated with CF_3PEAI showed an increased V_{oc} 0.73 V and a PCE of 10.35%, outperforming untreated devices [121]. Introducing 4-fluorophenethylamine hydrobromide (FPEABr) as an interfacial dipole in Sn PSCs molecules improves energy-level alignment between the perovskite and ICBA ETL, boosting the V_{oc} from 0.883 to 0.974 V. The resulting solar cell achieved a record PCE of 15.7%. UPS analysis confirmed favorable shifts in the perovskites VB (Figure 18H–J), attributed to the dipole moment of FPEABr, which effectively reduces V_{loss} and facilitates efficient charge separation [120]. Collectively, these approaches reduce non-radiative recombination and trap states, with V_{oc} gains ranging from 0.07 to 0.23 V, pushing Sn halide PSCs toward their theoretical limits. However, challenges such as scalability and ambient stability persist, necessitating further refinement of these interfacial techniques.

4.6 | Enhancement of FF Through the Suppression of Non-Radiative Recombination, Trap States, and Tin Oxidation

Tin halide PSCs commonly demonstrate low FFs, primarily attributable to the inherent instability of Sn^{2+} ions and the pronounced propensity for Sn-vacancy formation during the crystallization of the perovskite film. The oxidation of Sn^{2+} to Sn^{4+} , coupled with the low formation energy of Sn vacancies, results in a substantial density of deep-level defect states. These defects,

which include Sn vacancies and undercoordinated Sn sites, induce self-p-type doping and serve as highly efficient centers for non-radiative recombination, thereby impeding charge extraction. Furthermore, undercoordinated Sn sites readily interact with ambient oxygen, exacerbating defect-assisted recombination losses and consequently diminishing the device's FF. Addressing these challenges is critical for improving the FF in Sn halide PSCs. Verma et al. [123] demonstrated that an increase in interfacial defect density (IDD) significantly reduces the FF in $FASnI_3$ cells. Specifically, in an optimized $Sn(S_{0.92}Se_{0.08})_2$ -ETL device, elevating the IDD from 10^{10} to 10^{15} cm^{-2} resulted in a decrease in FF from 81.86% to 71.02%. Li et al. [76] identified that FF suppression in Sn perovskites predominantly arises from Sn^{2+} oxidation, trap-assisted recombination, and suboptimal film formation that induces shunting pathways and limits charge extraction. By incorporating 2-aminoethanethiol (AET) as an additive, which chemically stabilizes Sn^{2+} and modulates crystallization dynamics, they achieved a reduction in defect density from $1.52 \times 10^{16} \text{ cm}^{-3}$ (control) to $9.81 \times 10^{15} \text{ cm}^{-3}$ (AET-treated Sn halide perovskite). This approach also diminished dark current, enhanced film morphology, and improved interfacial charge transport, culminating in an FF of 80.26% (see Figure 19A,B).

An alternative approach was proposed by Sanchez-Diaz et al. [124], who introduced the secondary ammonium cation dipropylammonium iodide (DiPI) in conjunction with the reducing agent sodium borohydride ($NaBH_4$) to inhibit Sn^{2+} oxidation. This strategy yielded compact, pinhole-free films characterized by larger and more uniform grains, substantially mitigating trap-assisted recombination and enhancing PL lifetime (refer to Figure 19C,D). Thus, restricting Sn oxidation during solution processing and crystallization not only improves film morphology but also suppresses trap density, thereby enhancing device FF.

Wang et al. [125] employed cesium trifluoroacetate ($CsTFA$) as both an antioxidant and Lewis base additive. $CsTFA$ coordinates with Sn^{2+} ions and forms hydrogen bonds with formamidinium (FA^+), stabilizing the perovskite lattice and passivating defects. The addition of $CsTFA$ reduced the trap density from 4.15×10^{16} to $3.04 \times 10^{16} \text{ cm}^{-3}$, which corresponded to improvements in FF (68.8%) and V_{oc} (0.592 V) (see Figure 19E–G). Jia et al. [126] utilized semicarbazide hydrochloride (SEM-HCl) as a precursor additive, which chemically coordinates to undercoordinated Sn sites via the $O=C-N$ functional group. This coordination reduces surface Sn vacancies and inhibits oxygen adsorption, leading to a decrease in trap density from $3.52 \times 10^{16} \text{ cm}^{-3}$ (control) to $2.08 \times 10^{16} \text{ cm}^{-3}$ in SEM-HCl-assisted Sn perovskite films, thereby enhancing the FF to 67.97% (refer to Figure 19H–J).

5 | Challenges and Future Research Directions

5.1 | Overcoming the Fundamental Limitations of Sn Halide PSCs

The fundamental limitation of Sn halide perovskites stems from the chemical instability of the Sn^{2+} cation, which readily oxidizes to Sn^{4+} under ambient or mildly oxidative conditions. This oxidation disrupts the stoichiometry and electronic balance of the perovskite lattice, giving rise to a high density of Sn vacancies, self-p-type doping, and deep trap states, all of which

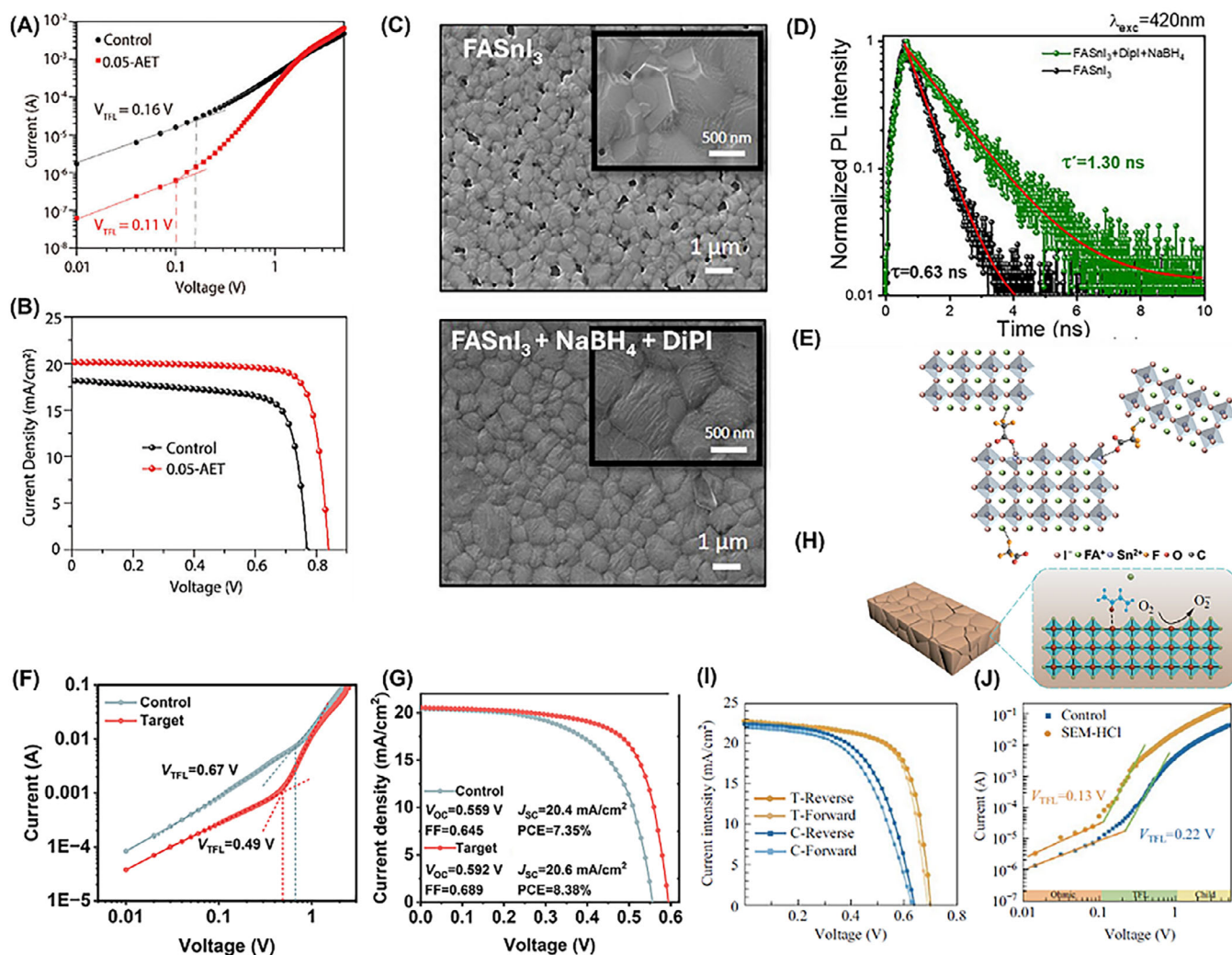


FIGURE 19 | (A and B) Space charge–limited current (SCLC) measurement of a hole-only device (FTO/PEDOT:PSS/perovskite/PTAA/Ag) and J – V characteristic curve for control and 0.05-AET Sn PSCs. (C and D) Top view of scanning electron microscopy (SEM) images and photoluminescence lifetime measurements of FASnI₃ (control) and FASnI₃ + NaBH₄ + DIPI perovskite films. (E) Schematic representation of chemical interaction of CsTFA with perovskite, (F and G) SCLC (electron-only device (ITO/SnO₂/perovskite/C₆₀/Ag)) and J – V characteristic curves for control and CsTFA-assisted PSCs. (H) Graphical representation of SEM-HCL additive interaction with perovskite; (I and J) J – V curve and trap density calculated through hole-only device. SEM-HCL, semicarbazide hydrochloride. *Source:* (A and B) Reproduced with permission [76]. Copyright 2023, John Wiley and Sons. (C and D) Reproduced with permission [124]. Copyright 2022, Joule. (E–G) Reproduced with permission [125]. Copyright 2024, Royal Society of Chemistry. (H–J) Reproduced with permission [126]. Copyright CC BY 4.0 International License.

serve as dominant centers for non-radiative recombination. These defect pathways collectively lead to substantial V_{loss} and FF loss. Future progress in Sn halide PSCs centers critically depends on mastering the chemistry of molecular coordination and solvent systems during film fabrication. Given the unique redox sensitivity and high reactivity of Sn²⁺, rational control over precursor solvent interactions is essential to suppress oxidation, modulate crystallization kinetics, and minimize defect formation. Emerging strategies in molecular coordination chemistry offer powerful avenues for stabilizing Sn²⁺ through the formation of robust precursor complexes. Future research should focus on designing multidentate or sterically hindered ligands that can effectively chelate Sn²⁺, preventing its oxidation during both solution processing and film crystallization. Incorporation of redox-inert Lewis bases with tailored donor strengths could also mitigate the disproportionation of Sn²⁺ while enabling controlled

nucleation and grain growth. The development of new solvent systems based on coordinative tunability can decouple coordination strength from redox activity. Ionic liquids, deep eutectic solvents, and fluorinated amides represent promising classes that warrant systematic investigation for their ability to form stable Sn complexes and promote uniform film morphology. Ultimately, advancing the understanding and control of coordination environments and solvent dynamics will be pivotal in overcoming the intrinsic instability of Sn halide perovskites. Such molecular-level innovations will lay the foundation for scalable, low-defect, and high-efficiency lead-free PSCs. Concurrently, achieving precise energy-level alignment within the CTLs is critical. This involves optimizing the LUMO and HOMO levels of the ETL and HTL, respectively, adjusting their work functions, and incorporating ultrathin cascade or buffer interlayers. Such modifications serve to eliminate energetic barriers that contribute to minority-carrier

accumulation and localized recombination. Consequently, these measures mitigate interfacial recombination, prevent the collapse of QFLS at interfaces, and facilitate efficient carrier extraction. Collectively, these strategies contribute to the reduction of trap densities, prolongation of carrier lifetimes, and enhancement of QFLS, thereby improving V_{oc} and FF in Sn-halide PSCs.

AI-augmented materials screening platforms can predict optimal passivating agents by learning structure–property relationships from experimental and DFT-computed databases. These tools can identify additives or interlayers that specifically suppress deep traps and reduce non-radiative recombination rates and enhance charge carrier mobility, thereby directly improving both V_{oc} and FF. Incorporating AI into real-time monitoring systems during fabrication can enable adaptive control of environmental conditions and film crystallization dynamics, thus reducing Sn^{2+} oxidation and vacancy formation. Such closed-loop systems could ensure consistent, high-quality film deposition under scalable manufacturing conditions.

Beyond the selection of materials, AI-driven device simulations employing ML frameworks, such as graph neural networks (GNNs), physics-informed ML (PIML), and Gaussian processes, offer promising avenues for optimizing the entire device architecture. Simulation methodologies encompass multi-parameter optimization, including perovskite layer thickness, CTL composition, buried interface engineering, interfacial energy-level alignment, and electrode design, all aimed at maximizing internal QFLS [52, 127]. For example, the development of novel AI-driven simulation strategies has the potential to substantially enhance V_{oc} and FF in tin-based devices. Specifically, AI-augmented SCAPS-1D models enable rapid exploration of the effects of perovskite absorber layer thickness, defect densities, doping concentrations, and interface characteristics on device performance, thereby facilitating the efficient identification of optimal device configurations [128]. By integrating AI across the domains of material discovery, process optimization, and device architecture design, researchers can accelerate the rational engineering of tin-based PSCs. This integrated approach aims to suppress non-radiative recombination losses, improve carrier extraction efficiency, and simultaneously enhance V_{oc} and FF, ultimately bridging the gap between laboratory-scale optimization and scalable manufacturing processes.

5.2 | Environmental and Commercial Viability of Sn Halide PSCs

Although Sn halide PSCs offer an environmentally friendlier profile compared to Pb-based systems, their commercial viability centers on the balance between performance, long-term operational stability, and eco-safety. From a toxicity standpoint, Sn poses less risk of bioaccumulation and groundwater contamination; however, Sn^{4+} and iodinated degradation products still pose environmental and electronic stability challenges. Ensuring environmental safety requires encapsulation techniques that can prevent oxidative degradation while maintaining efficient charge carrier transport. Furthermore, scalable and low-cost synthesis methods that minimize toxic solvent use, such as green antisolvents and solvent-free deposition, will be essential for translating lab-scale advances to commercial-scale modules.

To reach par with or surpass Pb-based PSCs in terms of PCE and durability, Sn halide PSCs must achieve V_{oc} values approaching the SQ limit. This necessitates not only material innovation but also system-level integration of compatible CTLs, stable electrodes, and flexible substrates. Recycling strategies and life-cycle assessments must also be integrated into the technology's development pipeline to ensure that Sn halide PSCs deliver on its sustainability promise. Interdisciplinary collaboration spanning materials science, environmental chemistry, device physics, and engineering will be crucial for addressing these multifaceted challenges. Ultimately, the future of Sn halide PSCs will be determined by the convergence of high-efficiency device architecture with scalable, stable, and safe deployment strategies.

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Conflicts of Interest

The authors declare no conflicts of interest.

References

1. S. M. Asnain, "Examining the Advances, Obstacles, and Achievements of Tin-Based Perovskite Solar Cells: A Review," *Solar Energy* 262 (2023): 111825.
2. J. Cao and F. Yan, "Recent Progress in Tin-Based Perovskite Solar Cells," *Energy & Environmental Science* 14, no. 3 (2021): 1286–1325.
3. W. Ke, C. C. Stoumpos, and M. G. Kanatzidis, "'Unleaded' Perovskites: Status Quo and Future Prospects of Tin-Based Perovskite Solar Cells," *Advanced Materials* 31, no. 47 (November 2019): e1803230.
4. W. F. Yang, F. Igbari, Y. H. Lou, Z. K. Wang, and L. S. Liao, "Tin Halide Perovskites: Progress and Challenges," *Advanced Energy Materials* 10, no. 13 (2019): 1902584.
5. M. Pitaro, E. K. Tekelenburg, S. Shao, and M. A. Loi, "Tin Halide Perovskites: From Fundamental Properties to Solar Cells," *Advanced Materials* 34, no. 1 (January 2022): e2105844.
6. L. Wang, H. Bi, J. Liu, et al., "Exceeding 15% Performance With Energy Level Tuning in Tin-Based Perovskite Solar Cells," *ACS Energy Letters* 9, no. 12 (2024): 6238–6244.
7. J. Chen, J. Luo, E. Hou, et al., "Efficient Tin-Based Perovskite Solar Cells With Trans-Isomeric Fulleropyrrolidine Additives," *Nature Photonics* 18, no. 5 (2024): 464–470.
8. S. Rühle, "Tabulated Values of the Shockley–Queisser Limit for Single Junction Solar Cells," *Solar Energy* 130 (2016): 139–147.
9. Z. Guo, A. K. Jena, G. M. Kim, and T. Miyasaka, "The High Open-Circuit Voltage of Perovskite Solar Cells: A Review," *Energy & Environmental Science* 15, no. 8 (2022): 3171–3222.
10. X. Jiang, F. Wang, Q. Wei, et al., "Ultra-High Open-Circuit Voltage of Tin Perovskite Solar Cells via an Electron Transporting Layer Design," *Nature Communications* 11, no. 1 (March 2020): 1245.
11. Y. Li, S. Yang, S. Yan, X. Liu, G. Shi, and T. He, "Open-Circuit Voltage Loss Management for Efficient Inverted Wide-Bandgap Perovskite Photovoltaics," *Advanced Functional Materials* 35, no. 7 (2024): 2415331.
12. M. Koopmans and L. J. A. Koster, "Voltage Deficit in Wide Bandgap Perovskite Solar Cells: The Role of Traps, Band Energies, and Effective Density of States," *Solar RRL* 6, no. 12 (2022): 2200560.

13. I. Elango, M. Selvamani, P. C. Ramamurthy, and A. V. Kesavan, "Studying VOC in Lead Free Inorganic Perovskite Photovoltaics by Tuning Energy Bandgap and Defect Density," *Ceramics International* 48, no. 19 (2022): 29414–29420.
14. D. Grabowski, Z. Liu, G. Schöpe, U. Rau, and T. Kirchartz, "Fill Factor Losses and Deviations From the Superposition Principle in Lead Halide Perovskite Solar Cells," *Solar RRL* 6, no. 11 (2022): 2200507.
15. N. Wu, Y. Wu, D. Walter, et al., "Identifying the Cause of Voltage and Fill Factor Losses in Perovskite Solar Cells by Using Luminescence Measurements," *Energy Technology* 5, no. 10 (2017): 1827–1835.
16. M. Stolterfoht, C. M. Wolff, Y. Amir, et al., "Approaching the Fill Factor Shockley–Queisser Limit in Stable, Dopant-Free Triple Cation Perovskite Solar Cells," *Energy & Environmental Science* 10, no. 6 (2017): 1530–1539.
17. S. M. Oner, D. Acikgoz, E. Sezen, et al., "Formation and Passivation of Surface Defects in Lead-Free Tin Halide Perovskites," *Journal of Physical Chemistry C* 128, no. 44 (2024): 18962–18967.
18. J. Zhang and Y. Zhong, "Origins of p-Doping and Nonradiative Recombination in CsSnI₃," *Angewandte Chemie, International Edition in English* 61, no. 44 (November 2022): e202212002.
19. P. Caprioglio, C. M. Wolff, O. J. Sandberg, et al., "On the Origin of the Ideality Factor in Perovskite Solar Cells," *Advanced Energy Materials* 10, no. 27 (2020): 2000502.
20. V. Sarritzu, N. Sestu, D. Marongiu, et al., "Optical Determination of Shockley–Read–Hall and Interface Recombination Currents in Hybrid Perovskites," *Scientific Reports* 7, no. 1 (March 2017): 44629.
21. C. Liu, Q. Zeng, and B. Yang, "Managing Energy Loss in Inorganic Lead Halide Perovskites Solar Cells," *Advanced Materials Interfaces* 6, no. 22 (2019): 1901136.
22. J. Warby, S. Shah, J. Thiesbrummel, et al., "Mismatch of Quasi-Fermi Level Splitting and Voc in Perovskite Solar Cells," *Advanced Energy Materials* 13, no. 48 (2023): 2303135.
23. W. Yang, H. Long, X. Sha, et al., "Unlocking Voltage Potentials of Mixed-Halide Perovskite Solar Cells via Phase Segregation Suppression," *Advanced Functional Materials* 32, no. 12 (2021): 2110698.
24. A. Razzaq, A. Ullah, A. S. Subbiah, and S. De Wolf, "Practical Fill Factor Limits for Perovskite Solar Cells," *ACS Energy Letters* 9, no. 11 (2024): 5635–5638.
25. X. Zhang, S. Wang, W. Zhu, Z. Cao, A. Wang, and F. Hao, "The Voltage Loss in Tin Halide Perovskite Solar Cells: Origins and Perspectives," *Advanced Functional Materials* 32, no. 8 (2021): 2108832.
26. D. Ricciarelli, D. Meggiolaro, F. Ambrosio, and F. De Angelis, "Instability of Tin Iodide Perovskites: Bulk p-Doping Versus Surface Tin Oxidation," *ACS Energy Letters* 5, no. 9 (2020): 2787–2795.
27. Y. Liang, X. Cui, F. Li, et al., "Origin of Enhanced Nonradiative Carrier Recombination Induced by Oxygen in Hybrid Sn Perovskite," *Journal of Physical Chemistry Letters* 14, no. 12 (March 2023): 2950–2957.
28. Z. Zhang, X. Tian, C. Wang, et al., "Revealing Superoxide-Induced Degradation in Lead-Free Tin Perovskite Solar Cells," *Energy & Environmental Science* 15, no. 12 (2022): 5274–5283.
29. D. Meggiolaro, D. Ricciarelli, A. A. Alasmari, F. A. S. Alasmari, and F. De Angelis, "Tin Versus Lead Redox Chemistry Modulates Charge Trapping and Self-Doping in Tin/Lead Iodide Perovskites," *Journal of Physical Chemistry Letters* 11, no. 9 (May 2020): 3546–3556.
30. A. K. Baranwal, H. Bi, G. Kapil, et al., "Enhanced Electron Transport in Heterojunction Sn-Perovskite Solar Cells Assisted by [6,6]-Phenyl-C61-Butyric Acid Methyl Ester as a Dopant," *ACS Energy Letters* 9, no. 8 (2024): 4119–4126.
31. Z. Zhang, L. Wang, H. Bi, et al., "Enhancement of Efficiency and Stability for Tin Halide Perovskite Solar Cells by Using Improved Doping Method," *Advanced Optical Materials* 12, no. 2 (2023): 2300962.
32. M. E. Kayesh, M. A. Karim, Y. He, Y. Shirai, M. Yanagida, and A. Islam, "Minimization of Energy Level Mismatch of PCBM and Surface Passivation for Highly Stable Sn-Based Perovskite Solar Cells by Doping n-Type Polymer," *Small* 20, no. 43 (October 2024): e2402896.
33. C. Liu, X. Zhen, W. Peng, et al., "CsSnI₃ Quantum Dots as a Multifunctional Interlayer for High-Efficiency Bilayer Perovskite Solar Cells," *Advanced Energy Materials* 15, no. 19 (2025): 2405074.
34. A. Abudulimu, S. Fu, N. Katakumbura, et al., "Enhanced Understanding of Recombination Mechanisms in High-Performance Tin-Lead Perovskite Solar Cells," *Cell Reports Physical Science* 6, no. 1 (2025): 102349.
35. S. Singh and D. Kabra, "Comparative Study of Recombination Dynamics in Optimized Composition of Sn-Versus Pb-Based Perovskite Solar Cells," *ACS Applied Materials & Interfaces* 13, no. 35 (September 2021): 42297–42306.
36. C. Sun, P. Yang, Z. Nan, et al., "Well-Defined Fullerene Bisadducts Enable High-Performance Tin-Based Perovskite Solar Cells," *Advanced Materials* 35, no. 9 (March 2023): e2205603.
37. H. Dong, R. Huang, W. Gao, et al., "Decoupling Nucleation and Growth of Crystal for DMSO-Free Self-Assembly Tin Perovskite Films and Their Optoelectronic Application," *Advanced Functional Materials* 35, no. 24 (2025): 2420593.
38. C. Wang, Y. Zhang, F. Gu, et al., "Illumination Durability and High-Efficiency Sn-Based Perovskite Solar Cell Under Coordinated Control of Phenylhydrazine and Halogen Ions," *Matter* 4, no. 2 (2021): 709–721.
39. C. S. Pathak, B.-J. Chang, and S. Song, "Review on Scanning Probe Microscopy Analysis for Perovskite Materials and Solar Cells," *Dyes and Pigments* 218 (2023): 111469.
40. A. Singh, J. Hieulle, J. F. Machado, et al., "Coevaporation Stabilizes Tin-Based Perovskites in a Single Sn-Oxidation State," *Nano Letters* 22, no. 17 (September 2022): 7112–7118.
41. J. Horn and D. Schlettwein, "Role of Interfaces and Contact Formation for the Application of Lead-Free Perovskite Materials in Photovoltaic Cells," *Physica Status Solidi (RRL)–Rapid Research Letters* 15, no. 11 (2021): 2100369.
42. M. Kumar, A. Raj, A. Kumar, and A. Anshul, "Computational Analysis of Bandgap Tuning, Admittance and Impedance Spectroscopy Measurements in Lead-Free MASnI₃ Perovskite Solar Cell Device," *International Journal of Energy Research* 46, no. 8 (2022): 11456–11469.
43. T. H. Chowdhury, R. Kaneko, T. Kaneko, K. Sodeyama, J.-J. Lee, and A. Islam, "Electronic Defect Passivation of FASnI₃ Films by Simultaneous Hydrogen-Bonding and Chlorine Co-Ordination for Highly Efficient and Stable Perovskite Solar Cells," *Chemical Engineering Journal* 431 (2022): 133745.
44. T. Yokoyama, Y. Nishitani, Y. Miyamoto, et al., "Improving the Open-Circuit Voltage of Sn-Based Perovskite Solar Cells by Band Alignment at the Electron Transport Layer/Perovskite Layer Interface," *ACS Applied Materials & Interfaces* 12, no. 24 (June 2020): 27131–27139.
45. Y. Jiang, Z. Zhang, Y. Wang, et al., "Crystallization Kinetics Regulation for Strain and Morphology Management Enables Efficient Tin Perovskite Solar Cells," *Advanced Functional Materials* 35, no. 31 (2025): 2504541.
46. K. Jin, Y. T. Yang, Y. Xia, et al., "Regenerative Redox Cycling Enables Stable Tin Perovskite Photovoltaics," *Advanced Materials* (September 2025): e14719.
47. Y. T. Yang, F. Hu, T. Y. Teng, et al., "Dual-Stage Reduction Strategy of Tin Perovskite Enables High Performance Photovoltaics," *Angewandte Chemie, International Edition in English* 64, no. 3 (January 2025): e202415681.
48. S. Joy, T. Hossain, A. Tichy, S. Johnson, and K. R. Graham, "Defect Modulation via SnX₂ Additives in FASnI₃ Perovskite Solar Cells," *Journal of Physical Chemistry Letters* 15, no. 14 (April 2024): 3851–3858.
49. X. Zhou, W. Peng, Z. Liu, et al., "Additive Engineering With 2,8-Dibromo-Dibenzothiophene-S,S-Dioxide Enabled Tin-Based Perovskite Solar Cells With 14.98% Power Conversion Efficiency," *Energy & Environmental Science* 17, no. 8 (2024): 2837–2844.

50. T. Y. Teng, Z. H. Su, F. Hu, et al., "Electronically Manipulated Molecular Strategy Enabling Highly Efficient Tin Perovskite Photovoltaics," *Angewandte Chemie, International Edition in English* 63, no. 7 (February 2024): e202318133.
51. M. Hasanzadeh Azar, S. Ayneband, and H. Abdollahi, "SCAPS Empowered Machine Learning Modelling of Perovskite Solar Cells: Predictive Design of Active Layer and Hole Transport Materials," *Photonics* 10, no. 3 (2023): 271.
52. W.-Y. Gao, C.-X. Ran, L. Zhao, et al., "Machine Learning Guided Efficiency Improvement for Sn-Based Perovskite Solar Cells With Efficiency Exceeding 20%," *Rare Metals* 43, no. 11 (2024): 5720–5733.
53. T. M. Khan and S. R. A. Ahmed, "Investigating the Performance of FASnI₃-Based Perovskite Solar Cells With Various Electron and Hole Transport Layers: Machine Learning Approach and SCAPS-1D Analysis," *Advanced Theory and Simulations* 7, no. 10 (2024): 2400353.
54. A. I. Shimul, M. A. Khan, A. Rayhan, and A. Ghosh, "Machine Learning-Based Optimization and Performance Enhancement of CH₃NH₃SnBr₃ Perovskite Solar Cells With Different Charge Transport Materials Using SCAPS-1D and wxAMPS," *Advanced Theory and Simulations* 8 (2025): 2500182.
55. Z. Zhang, Y. Huang, C. Wang, et al., "Green-Antisolvent-Regulated Distribution of P-Type Self-Doping Enables Tin Perovskite Solar Cells With an Efficiency of Over 14%," *Energy & Environmental Science* 16, no. 8 (2023): 3430–3440.
56. D. Di Girolamo, J. Pascual, M. H. Aldamasy, et al., "Solvents for Processing Stable Tin Halide Perovskites," *ACS Energy Letters* 6, no. 3 (2021): 959–968.
57. X. Zhang, Y. Liu, X. Chen, et al., "Improved Perovskite Crystallization by Antisolvent Engineering in Tin-Perovskite Photovoltaics," *Physical Chemistry Chemical Physics* 26, no. 45 (November 2024): 28715–28723.
58. Y. Su, J. Yang, G. Liu, et al., "Acetic Acid-Assisted Synergistic Modulation of Crystallization Kinetics and Inhibition of Sn²⁺ Oxidation in Tin-Based Perovskite Solar Cells," *Advanced Functional Materials* 32, no. 12 (2021): 2109631.
59. H. Ban, T. Zhang, X. Gong, et al., "Fully Inorganic CsSnI₃ Mesoporous Perovskite Solar Cells With High Efficiency and Stability via Coadditive Engineering," *Solar RRL* 5, no. 7 (2021): 2100069.
60. C. Yuan, J. Wang, Y. Yang, et al., "Regulated Crystallization Through Intermolecular Interactions Bridging for Efficient Tin-Based Perovskite Solar Cells," *Small* 21, no. 8 (February 2025): e2408302.
61. T. Wang, H. L. Loi, Q. Cao, et al., "Counter-Doping Effect by Trivalent Cations in Tin-Based Perovskite Solar Cells," *Advanced Materials* 36, no. 30 (July 2024): e2402947.
62. L. Huang, W. Zheng, W. Zhang, et al., "Efficient Tin(II) Fluoride-Free Formamidinium Tin Triiodide Perovskite Solar Cells via Composition and Additive Engineering," *Solar RRL* 6, no. 12 (2022): 2200859.
63. Z. Zhao, M. Sun, Y. Ji, et al., "Efficient Homo Junction Tin Perovskite Solar Cells Enabled by Gradient Germanium Doping," *Nano Letters* 24, no. 18 (May 2024): 5513–5520.
64. J. Choi, J. Kim, M. Jeong, et al., "Molecularly Engineered Alicyclic Organic Spacers for 2D/3D Hybrid Tin-Based Perovskite Solar Cells," *Small* 20, no. 48 (November 2024): e2405598.
65. M. Sun, M. Ma, Y. Guo, et al., "Difluorine-Substituted Molecule-Based Low-Dimensional Structure for Highly Stable Tin Perovskite Solar Cells," *Solar RRL* 6, no. 11 (2022): 2200672.
66. B. Chang, L. Wang, H. Li, et al., "Phase-Pure 2D/3D Tin-Based Perovskite Films for Solar Cells," *ACS Energy Letters* 9, no. 2 (2024): 363–372.
67. F. Du, H. Gu, W. Jiang, et al., "Managing Crystallization and Phase Distribution via 2D Perovskite Seed Crystals for 2D-3D Tin-Based Perovskite Solar Cells," *Advanced Functional Materials* 35, no. 3 (2024): 2413281.
68. B. Chang, B. Li, Z. Wang, et al., "Efficient Bulk Defect Suppression Strategy in FASnI₃ Perovskite for Photovoltaic Performance Enhancement," *Advanced Functional Materials* 32, no. 12 (2021): 2107710.
69. W. Gao, R. Huang, H. Dong, et al., "Heteroatomic Molecules for Coordination Engineering Towards Advanced Pb-Free Sn-Based Perovskite Photovoltaics," *Chemical Society Reviews* 54, no. 3 (February 2025): 1384–1428.
70. Q. Tai, X. Guo, G. Tang, et al., "Antioxidant Grain Passivation for Air-Stable Tin-Based Perovskite Solar Cells," *Angewandte Chemie, International Edition in English* 58, no. 3 (January 2019): 806–810.
71. G. Li, Z. Su, M. Li, et al., "Ionic Liquid Stabilizing High-Efficiency Tin Halide Perovskite Solar Cells," *Advanced Energy Materials* 11, no. 32 (2021): 2101539.
72. B. Li, H. Di, B. Chang, et al., "Efficient Passivation Strategy on Sn Related Defects for High Performance All-Inorganic CsSnI₃ Perovskite Solar Cells," *Advanced Functional Materials* 31, no. 11 (2021): 2007447.
73. Z. Zhang, H. Yu, J. Huang, et al., "Over 12% Efficient CsSnI₃ Perovskite Solar Cells Enabled by Surface Post-Treatment With Bi-Functional Polar Molecules," *Chemical Engineering Journal* 490 (2024): 151561.
74. S. Zhong, Z. Li, C. Zheng, et al., "Guanidine Thiocyanate-Induced High-Quality Perovskite Film for Efficient Tin-Based Perovskite Solar Cells," *Solar RRL* 6, no. 7 (2022): 2200088.
75. Z. Zhu, X. Jiang, D. Yu, N. Yu, Z. Ning, and Q. Mi, "Smooth and Compact FASnI₃ Films for Lead-Free Perovskite Solar Cells With Over 14% Efficiency," *ACS Energy Letters* 7, no. 6 (2022): 2079–2083.
76. T. Li, Z. Zhang, F. He, et al., "Alleviating the Crystallization Dynamics and Suppressing the Oxidation Process for Tin-Based Perovskite Solar Cells With Fill Factors Exceeding 80 Percent," *Advanced Functional Materials* 33, no. 51 (2023): 2308457.
77. M. E. Kayesh, Y. He, M. A. Karim, et al., "Optimization of Crystal Growth and Defect Passivation of FASnI₃ Film by Using 2-Pyridylthiourea for Sn-Based Perovskite Solar Cells," *ACS Applied Energy Materials* 8, no. 4 (2025): 2043–2049.
78. O. E. Solis, M. Minguez-Avellan, P. F. Betancur, et al., "Adjusting the Crystallization of Tin Perovskites Through Thiophene Additives for Improved Photovoltaic Stability," *ACS Energy Letters* 9, no. 11 (November 2024): 5288–5295.
79. P. Pandey, S. Cho, J. Bahadur, et al., "4-Phenylthiosemicarbazide Molecular Additive Engineering for Wide-Bandgap Sn Halide Perovskite Solar Cells With a Record Efficiency Over 12.2%," *Advanced Energy Materials* 14, no. 25 (2024): 2401188.
80. X. Ren, S. Wang, H. Cai, et al., "Multifunctional Acetaminophen Interlayer for High Efficiency and Durability Lead-Lean Perovskite Solar Cells," *Langmuir* 40, no. 38 (September 2024): 19905–19916.
81. W. Li, W. Gao, R. Huang, et al., "Homogenizing Nucleation and Growth of Tin Perovskite by Polarity-Free Trithiane Coordination Molecule for Efficient and Stable Photovoltaics," *Nano Letters* 24, no. 50 (December 2024): 16081–16089.
82. S. Wang, L. Yan, W. Zhu, et al., "Suppressing the Formation of Tin Vacancy Yields Efficient Lead-Free Perovskite Solar Cells," *Nano Energy* 99 (2022): 107416.
83. H. Jang, H. Y. Lim, Y. J. Yoon, et al., "Formate as Anti-Oxidation Additives for Pb-Free FASnI₃ Perovskite Solar Cells," *Solar RRL* 6, no. 12 (2022): 2200789.
84. G. Liu, Y. Zhong, W. Feng, et al., "Multidentate Chelation Heals Structural Imperfections for Minimized Recombination Loss in Lead-Free Perovskite Solar Cells," *Angewandte Chemie, International Edition in English* 61, no. 40 (October 2022): e202209464.
85. S. Cho, H. Song, P. Pandey, et al., "Carboxylate Pseudo-Halide-Assisted Crystallization and Antioxidant Strategy for Stable Wide Bandgap Tin Perovskite Photovoltaics," *Chemical Engineering Journal* 497 (2024): 154720.

86. A. Balilonda, M. Du, Z. Li, et al., "High Performance and Efficiency Recovery in Sn-Based Flexible Perovskite Solar Cells by Antioxidant Vanillin and Microwave Treatment," *Advanced Functional Materials* 34, no. 19 (2024): 2313833.
87. W. Zhang, Y. Cai, H. Liu, et al., "Organic-Free and Lead-Free Perovskite Solar Cells With Efficiency Over 11%," *Advanced Energy Materials* 12, no. 42 (2022): 2202491.
88. S. Zou, S. Ren, Y. Jiang, et al., "Efficient Environment-Friendly Lead-Free Tin Perovskite Solar Cells Enabled by Incorporating 4-Fluorobenzylammonium Iodide Additives," *Energy and Environmental Materials* 6, no. 6 (2023): e12465.
89. B. Chang, H. Li, L. Wang, et al., "Molecular Ferroelectric With Directional Polarization Field for Efficient Tin-Based Perovskite Solar Cells," *Advanced Functional Materials* 33, no. 50 (2023): 2305852.
90. C. Duan, F. Zou, Q. Wen, et al., "A Bifunctional Carbazide Additive for Durable CsSnI₃ Perovskite Solar Cells," *Advanced Materials* 35, no. 26 (June 2023): e2300503.
91. D. D. Mishra, P. K. Rath, N. Thirugnanam, et al., "Realizing SnF₂-TMAH Passivated Lead-Free Formamidinium Perovskite Solar Cells With Doctor-Bladed Carbon Electrode," *Progress in Photovoltaics: Research and Applications* 32, no. 8 (2024): 569–578.
92. J. Liu, S. Wang, W. Zhu, Z. Tang, L. Ding, and F. Hao, "Highly Symmetric Lewis Base Coordinated With Sn²⁺ for Reducing Voltage Loss and Retarding Oxidation in Tin-Halide Perovskite Solar Cells," *Chemical Engineering Journal* 453 (2023): 139975.
93. H. Yu, Z. Zhang, H. Ban, et al., "Deep Level Defect Passivation for Printable Mesoporous CsSnI₃ Perovskite Solar Cells With Efficiency Above 10%," *Journal of Energy Chemistry* 102 (2025): 10–17.
94. T. Li, Y. Wang, W. Zhu, et al., "Synergistic Effect of Two Hydrochlorides Resulting in Significantly Enhanced Performance of Tin-Based Perovskite Solar Cells With 3D to Quasi-2D Structural Transition," *Journal of Materials Chemistry A* 10, no. 27 (2022): 14441–14450.
95. J. Jin, Z. Zhang, S. Zou, et al., "Regulating Compressive Strain Enables High-Performance Tin-Based Perovskite Solar Cells," *Advanced Energy Materials* 15, no. 14 (2024): 2403718.
96. H. Li, X. Jiang, Q. Wei, et al., "Low-Dimensional Inorganic Tin Perovskite Solar Cells Prepared by Templated Growth," *Angewandte Chemie, International Edition in English* 60, no. 30 (July 2021): 16330–16336.
97. J. Zhou, M. Hao, Y. Zhang, et al., "Chemo-Thermal Surface Dedoping for High-Performance Tin Perovskite Solar Cells," *Matter* 5, no. 2 (2022): 683–693.
98. D. B. Khadka, Y. Shirai, R. Sahara, M. Yanagida, and K. Miyano, "Ameliorating Defects in Wide Bandgap Tin Perovskite Solar Cells Using Fluorinated Solvent and Hydrazide," *Small* 21, no. 17 (April 2025): e2410048.
99. P. F. Chan, M. Qin, C. J. Su, et al., "iso-BAI Guided Surface Recrystallization for Over 14% Tin Halide Perovskite Solar Cells," *Advancement of Science* 11, no. 22 (June 2024): e2309668.
100. G. Liu, X. Jiang, Y. He, et al., "Halogen Radical-Activated Perovskite-Substrate Buried Heterointerface for Achieving Hole Transport Layer-Free Tin-Based Solar Cells With Efficiencies Surpassing 14," *Angewandte Chemie, International Edition in English* 64, no. 7 (February 2025): e202419183.
101. C. H. Kuan, R. Balasaravanan, S. M. Hsu, et al., "Dopant-Free Pyrrolopyrrole-Based (PPr) Polymeric Hole-Transporting Materials for Efficient Tin-Based Perovskite Solar Cells With Stability Over 6000 h," *Advanced Materials* 35, no. 23 (June 2023): e2300681.
102. J. Ferdous, M. E. Kayesh, W. Jevasuwan, N. Fukata, and A. Islam, "Solution-Processed SnOx as a Hole-Transporting Material for Stable Sn-Based Perovskite Solar Cell," *Solar RRL* 9, no. 7 (2025): 2500047.
103. T. Mahmoudi, M. Kohan, W. Y. Rho, Y. Wang, Y. H. Im, and Y. B. Hahn, "Tin-Based Perovskite Solar Cells Reach Over 13% With Inclusion of N-Doped Graphene Oxide in Active, Hole-Transport, and Interfacial Layers," *Advanced Energy Materials* 12, no. 43 (2022): 2201977.
104. J. Chen, X. Zhao, Y. Cheng, et al., "Hydroxyl-Rich D-Sorbitol to Address Transport Layer/Perovskite Interfacial Issues Toward Highly Efficient and Stable 2D/3D Tin-Based Perovskite Solar Cells," *Advanced Optical Materials* 9, no. 22 (2021): 2100755.
105. K. Cao, H. Ning, N. Xu, et al., "Tailoring the Buried Interface With Self-Assembled 2-Chloroethylphosphonic Acid for Defect Reduction and Improved Performance of Tin-Based Perovskite Solar Cells," *Journal of Materials Chemistry A* 12, no. 28 (2024): 17444–17452.
106. J. Ryu, P. Pandey, S. Yoon, et al., "Enhanced Tin Halide Perovskite Solar Cells via Crystal Growth Control Using a Multifunctional Interfacial Modifier," *Journal of Materials Chemistry A* 13, no. 11 (2025): 8083–8095.
107. J. Qu, X. Wang, C. Luo, et al., "Enhancing Charge Collection of Tin-Based Perovskite Solar Cells by Optimizing the Buried Interface With a Multifunctional Self-Assembled Monolayer," *ACS Applied Materials & Interfaces* 17, no. 13 (April 2025): 19783–19794.
108. X. Liu, Y. Wang, F. Xie, X. Yang, and L. Han, "Improving the Performance of Inverted Formamidinium Tin Iodide Perovskite Solar Cells by Reducing the Energy-Level Mismatch," *ACS Energy Letters* 3, no. 5 (2018): 1116–1121.
109. C. Ran, J. Xi, W. Gao, et al., "Bilateral Interface Engineering Toward Efficient 2D–3D Bulk Heterojunction Tin Halide Lead-Free Perovskite Solar Cells," *ACS Energy Letters* 3, no. 3 (2018): 713–721.
110. S. Vegiraju, W. Ke, P. Priyanka, et al., "Benzodithiophene Hole-Transporting Materials for Efficient Tin-Based Perovskite Solar Cells," *Advanced Functional Materials* 29, no. 45 (2019): 1905393.
111. D. Song, S. Ramakrishnan, Y. Zhang, and Q. Yu, "Mixed Self-Assembled Monolayers for High-Photovoltage Tin Perovskite Solar Cells," *ACS Energy Letters* 9, no. 4 (2024): 1466–1472.
112. Y. Ma, J. Wu, Z. Wu, M. H. Mahyuddin, and Z. Liang, "Multifaceted Reductant for Buried Interface Modification of Tin-Based Perovskite Solar Cells by Concurrently Suppressing Sn-Oxidation and Facilitating Energy-Alignment," *Advanced Functional Materials* (2025): e12300.
113. H. Na, S. Alam, G. Ham, et al., "Interlayer Molecular Doping to Enhance Efficiency in Tin Perovskite Solar Cells," *ACS Energy Letters* 9, no. 9 (2024): 4306–4315.
114. L. Wang, Q. Miao, D. Wang, et al., "Ternary Passivation for Enhanced Carrier Transport and Recombination Suppression in Highly Efficient Sn-Based Perovskite Solar Cells," *Small* 20, no. 46 (November 2024): e2404026.
115. F. He, T. Li, T. Shen, et al., "Hydrophobic Electron-Transport Layer for Efficient Tin-Based Perovskite Solar Cells," *Advanced Functional Materials* 34, no. 40 (2024): 2405611.
116. M. Sun, Z. Zhao, H. Xu, et al., "Boosting Tin Perovskite Solar Cell Performance via Light-Induced Interface Doping," *Nano Letters* 25, no. 8 (February 2025): 3103–3112.
117. W. Ke, C. C. Stoumpos, J. L. Logsdon, et al., "TiO₂-ZnS Cascade Electron Transport Layer for Efficient Formamidinium Tin Iodide Perovskite Solar Cells," *Journal of the American Chemical Society* 138, no. 45 (November 2016): 14998–15003.
118. C. Sun, H. Zhang, S. Cheng, et al., "Multidentate Fullerenes Enable Tunable and Robust Interfacial Bonding for Efficient Tin-Based Perovskite Solar Cells," *Advanced Materials* 36, no. 44 (November 2024): e2410248.
119. J. Chen, J. Luo, Y. Li, et al., "Spatially Isomeric Fulleropyrrolidines Enable Controlled Stacking of Perovskite Colloids for High-Performance Tin-Based Perovskite Solar Cells," *Angewandte Chemie, International Edition in English* 64, no. 7 (February 2025): e202420150.
120. Y. Shi, Z. Zhu, D. Miao, Y. Ding, and Q. Mi, "Interfacial Dipoles Boost Open-Circuit Voltage of Tin Halide Perovskite Solar Cells," *ACS Energy Letters* 9, no. 4 (2024): 1895–1897.

121. B. Chen, S. Wang, X. Zhang, W. Zhu, Z. Cao, and F. Hao, "Reducing the Interfacial Voltage Loss in Tin Halides Perovskite Solar Cells," *Chemical Engineering Journal* 445 (2022): 136769.
122. S. Yoon, T.-J. Ha, and D.-W. Kang, "Improving the Performance and Reliability of Inverted Planar Perovskite Solar Cells With a Carbon Nanotubes/PEDOT: PSS Hybrid Hole Collector," *Nanoscale* 9, no. 27 (2017): 9754–9761.
123. A. A. Verma and D. K. Dwivedi, "Revolutionizing Environment Friendly FASnI₃ Perovskite Solar Cells With Pioneering Selenium Doped Metal Chalcogenide Charge Transport Layer Unlocking 32% Efficiency," *Scientific Reports* 15, no. 1 (July 2025): 27473.
124. J. Sanchez-Diaz, R. S. Sanchez, S. Masi, et al., "Tin Perovskite Solar Cells With >1300 h of Operational Stability in N(2) Through a Synergistic Chemical Engineering Approach," *Joule* 6, no. 4 (April 2022): 861–883.
125. J. Wang, H. Dong, Z. Chen, et al., "Mitigating Sn²⁺ Oxidation and Enhancing Device Performance in Tin-Based Perovskite Solar Cells via a CsTFA Additive Strategy," *Sustain Energ Fuels* 9, no. 17 (2025): 4674–4680.
126. W. Jia, Y. Jing, H. Zhang, et al., "Suppression of Deep-Level Traps via Semicarbazide Hydrochloride Additives for High-Performance Tin-Based Perovskite Solar Cells," *Front Optoelectron* 16, no. 1 (December 2023): 47.
127. Q. Zhang, H. Wang, Q. Zhao, et al., "Machine-Learning-Assisted Design of Buried-Interface Engineering Materials for High-Efficiency and Stable Perovskite Solar Cells," *ACS Energy Letters* 9, no. 12 (2024): 5924–5934.
128. S. Farhan, M. Q. Shah, M. N. Khan, M. Arif, and A. Ghafoor, "Exploring the Bilayer Approach to Analyzing Lead-Free Perovskite Solar Cells' Numerical Aspects for High Efficiency," *Journal of Optics and Photonics Research* 1, no. 4 (2024): 190–201.