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Chelating Coordination Regulates Perovskite Crystallization and Defect Passivation in Sn–Pb Perovskite Solar Cells

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ABSTRACT

Tin-lead (Sn–Pb) perovskite (TLP) serve as potential narrow-bandgap absorbers for photovoltaics; unfortunately, issues such as uncontrolled crystallization, Sn^{2+} oxidation, and interfacial defects continue to limit device efficiency and stability. In this study, we present a chelating coordination strategy at buried and top perovskite interface utilizing ethylenediamine diacetate (EDDA) to synergistically regulate perovskite crystallization and defect passivation in TLP. Post-treatment of PEDOT:PSS using EDDA mitigates surface acidity and reduces insulating PSS-rich domains through ionic exchange, thereby shifting the buried interface potential. The carboxylate ($-\text{COO}^-$) groups of EDDA coordinate with undercoordinated $\text{Pb}^{2+}/\text{Sn}^{2+}$ cations, while the $-\text{NH}_3^+$ groups form hydrogen bonds in TLP. These interactions at buried interface reduce nucleation concentration and promote homogeneous and orderly (100)-facet crystal growth across TLP films. The chemical polishing of the TLP top surface inhibits the Sn^{2+} oxidation, reduces defects and facilitates more efficient charge extraction. As a result, the Target devices demonstrate a power conversion efficiency (PCE) of 23.30% (0.09 cm^2), with an enhanced open-circuit voltage of 0.877 V and a fill factor of 81.81%. Importantly, the Target device shows high stability for 300 s under continuous sunlight at maximum power point tracking and maintains 90% efficiency after 1800 h of storage in N_2 .

1 | Introduction

Organic–inorganic hybrid-based perovskite solar cells (PSCs) have emerged as a clean energy source because of their excellent optoelectronic properties and the ability to be processed at low temperatures [1]. Significant attempts have been made in recent years to enhance the performance of PSCs. The power conversion efficiencies (PCEs) of single-junction lead (Pb)-based PSC have been achieved over 27% [2]. Despite their remarkable potential, Pb-based perovskite possess an intrinsic bandgap ($\sim 1.5 \text{ eV}$) that exceeds the Shockley–Queisser ideal range (1.1–1.3 eV) for single-junction devices, thereby limiting the theoretical efficiency limit [3, 4]. To address this limitation, the partial substitution of Pb^{2+}

with tin (Sn^{2+}) in the perovskite lattice has been shown to be an efficient method for reducing the bandgap and extends the absorption edge toward the near-infrared region. The typical $\text{Sn}_{0.5}\text{Pb}_{0.5}$ composition provides an optimal bandgap of $\sim 1.25 \text{ eV}$, suitable for both single-junction operation and as the bottom absorber in all-perovskite tandem architectures [5]. In addition, substituting part of the toxic Pb with the more environmentally friendly Sn also supports the long-term sustainability of perovskite photovoltaics. Despite these advantages, mixed Sn–Pb perovskite (TLP) still face serious challenges due to present of Sn^{2+} ions. The Sn^{2+} ions is chemically unstable and easily oxidized to Sn^{4+} ions in the presence of oxygen or moisture [6]. This oxidation produces deep-level defects, self-doping, and high

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trap-assisted recombination, leading to rapid degradation of the device performance and stability. Moreover, the crystallization behavior of TLPs strongly depends on the underlying layer [7, 8]. The interface between the charge transport layer and the perovskite absorber is called buried interface. An uncontrolled crystallization on buried interface has exhibited the inhomogeneous nucleation, poor surface coverage, and rough morphology, resulting in high defect density and nonradiative losses [9–12].

Among the available hole transport layers (HTLs), poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS) has been widely used because of its excellent conductivity, optical transparency, and good energy-level matching with perovskites. Devices using PEDOT:PSS have achieved high PCEs, confirming its potential as a scalable HTL [9, 10, 13]. However, PEDOT:PSS has intrinsic drawbacks that limit its use in Sn-based systems. The acidic environment accelerates the Sn^{2+} oxidation and interfacial corrosion, while the insulating PSS-rich domains reduce carrier extraction and promote interfacial recombination [14]. In addition, phase segregation between PEDOT and PSS introduces structural inhomogeneity, resulting in heterogeneous perovskite nucleation, poor grain coverage, and low crystallinity at the buried interface of PEDOT:PSS/perovskite. The low-quality crystal at buried interface exhibits a greater number of deep-level defects in comparison to the upper interface, which potentially lead to degrading the device fill factor (FF) and open circuit voltage (V_{oc}) [8, 15].

To address these issues, defect passivation and interfacial engineering have emerged as crucial approaches for attaining efficient and stable Sn–Pb PSCs. Passivation approaches are often classified into three levels: (i) bulk defect passivation to suppress Sn vacancy and oxidation through reducing agents or excess halide; [16, 17] (ii) surface passivation to mitigate trap states and nonradiative recombination using Lewis bases, organic cations, or fullerene derivatives; [18, 19, 20] and (iii) buried interface passivation to regulate nucleation, improve adhesion, and tune interfacial energy alignment [7, 8, 21]. However, most reported strategies focus on either the top perovskite surface or the buried HTL/perovskite interface independently, leaving the synergistic interplay between both interfaces largely unexplored. The tailored modification of the PEDOT:PSS HTL has recently garnered attention as an approach to enhancing buried interface quality and reducing interfacial defects. Song et al. presented diammonium acetate salts as a post-treatment agent, demonstrating that the synergistic effects of $-\text{NH}_3^+$ and Ac^- ($-\text{COO}^-$) functionalities selectively etched excess insulating PSS and promoted strong electrostatic anchoring with the PEDOT-rich domains [14]. Lee et al. reported a cooperative methylammonium iodide/ dimethyl sulfoxide (MAI/DMSO) post-treatment method, showing that DMSO selectively coordinates with PSS-rich domains, while MA^+ and I^- ions function as ionic bridges that improve chemical binding between PEDOT:PSS and the perovskite absorber [22]. Zhang and colleagues recently used pentylammonium acetate (PenAAc) for the passivation of the PEDOT:PSS surface [15]. Density functional theory and experimental evidence indicate that PenA^+ and Ac^- groups decrease interfacial defect states and strengthen the chemical coupling between PEDOT:PSS and the Sn–Pb perovskite layer, leading to improved perovskite films quality and charge extraction. Recently, some studies have introduced dual molecule passivation strategies in which separate

modifiers are applied to the buried and surface interfaces to mitigate defects and improve interfacial charge transportation [8, 23]. A comprehensive approach that simultaneously addresses both interfaces using a multifunctional molecule could promote uniform crystallization, offer more effectively defect control, and stabilize the oxidation state of Sn^{2+} .

In this work, we introduce a chelating coordination strategy to simultaneously regulate perovskite crystallization and suppress defect formation in TLP solar cells. This strategy synergistically reduces the nucleation concentration at buried interface and passivates defects at top perovskite surface through the combined effects of chelating coordination and hydrogen bonding. Post-treatment of PEDOT:PSS with ethylenediamine diacetate (EDDA) mitigates surface acidity and reduces insulating PSS-rich domains through ionic exchange, thereby shifting the buried interface potential. As a multifunctional chelating molecule, EDDA regulates the perovskite crystallization by coordinating its carboxylate ($-\text{COO}^-$) groups with undercoordinated $\text{Pb}^{2+}/\text{Sn}^{2+}$ cations, while the protonated amine ($-\text{NH}_3^+$) groups form hydrogen bonds with the perovskite lattice. In addition, EDDA induces a chemical polishing effect that effectively passivates defect states at the top perovskite surface. This synergistic interfacial and surface modification improves perovskite films quality from the buried interface upward, leading to reduced trap densities, suppressing Sn^{2+} oxidation, and reducing non-radiative recombination losses. Consequently, the Target devices showed impressive PCE of 23.30% with high fill factor of 81.81%. Most importantly, the Target devices showed high stability at MPPT under continuous one sunlight illumination and for storage in N_2 environment.

2 | Results and Discussion

We used 1.27 eV mixed TLP featuring the composition $\text{FA}_{0.6}\text{MA}_{0.3}\text{Cs}_{0.1}\text{Pb}_{0.5}\text{Sn}_{0.5}\text{I}_3$ with 10% SnF_2 of SnI_2 as light absorber. The ethylenediamine diacetate (EDDA) salt was introduced in two steps: post-treated (i) the PEDOT:PSS HTL and (ii) TLP layer. The post-treatment process of PEDOT:PSS is shown in Figure S1. The pure PEDOT:PSS HTL defined as “PEDOT:PSS”, while EDDA post-treated PEDOT:PSS is defined as “PEDOT:PSS w/ EDDA”. Perovskite films deposited on PEDOT:PSS and PEDOT:PSS w/ EDDA are defined as “Control” and “Bottom”, respectively. The perovskite layer deposited on PEDOT:PSS w/ EDDA and subsequently post-treated with EDDA is defined as “Target”.

We initially examined the effect of EDDA modification on the surface properties of PEDOT:PSS HTL, followed by its impact on the crystallization dynamic of TLP films. Figure 1a illustrates the chemical structure of EDDA molecules, featuring a conjugated structure with two terminals ammonium ($-\text{NH}_3^+$) groups and two symmetrically positioned carboxylate ($-\text{COO}^-$ ($-\text{Ac}^-$)) groups. The bifunctional EDDA have both positive ($-\text{NH}_3^+$) and negative ($-\text{Ac}^-$) electronegative groups, enabling versatile chemical interaction with PEDOT:PSS and perovskite lattices through hydrogen bonding and chelating coordination [15, 24, 25]. The EDDA molecule dissolved in DMSO solvent could play hypothetically three critical roles during post-treatment of PEDOT:PSS HTL i.e., (i) remove excess PSS from the PEDOT:PSS

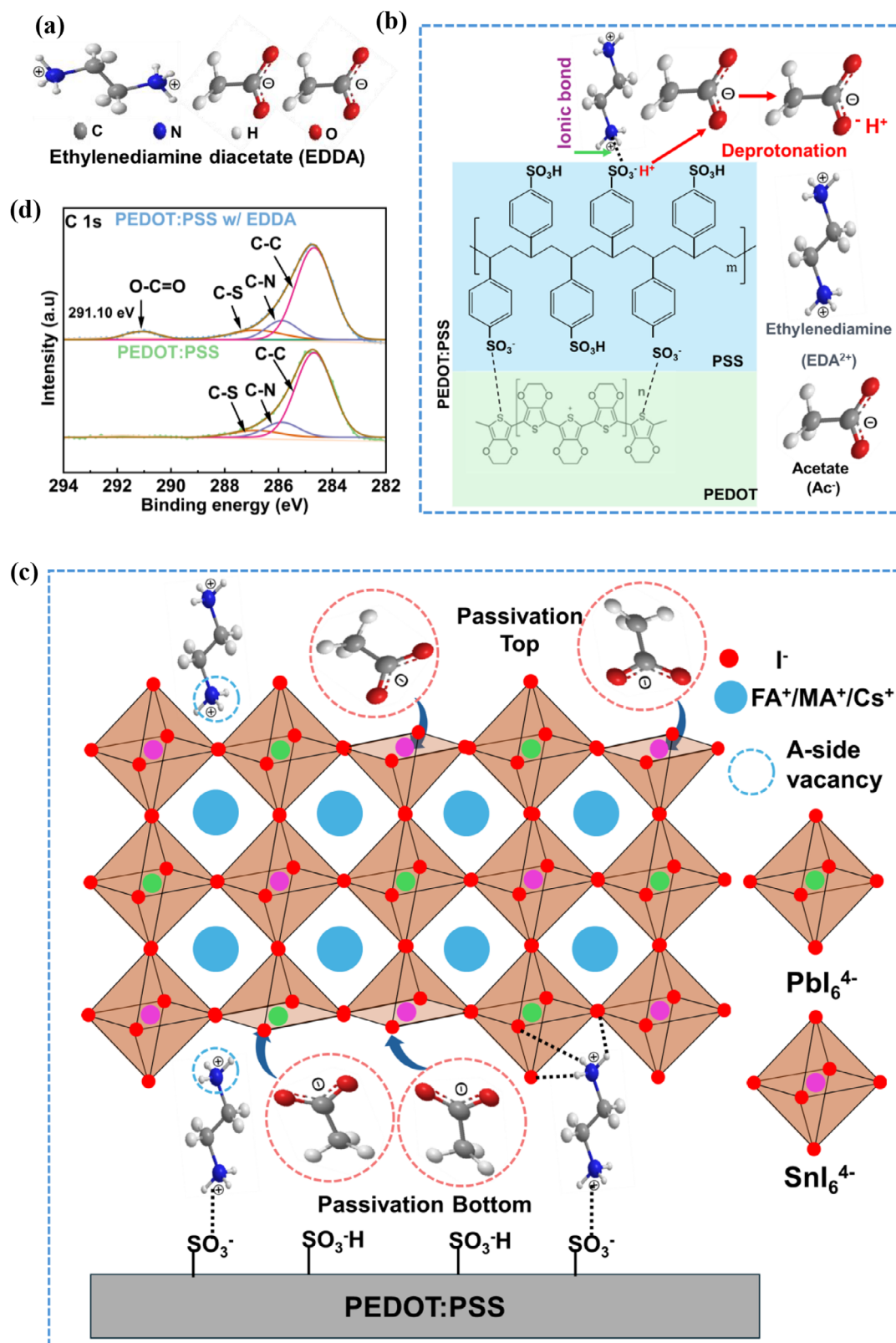


FIGURE 1 | a) Chemical structure of EDDA. b) Schematic presentation of the EDDA post-treatment mechanism onto the PEDOT:PSS HTL. c) Schematic presentation of the passivation mechanism for both the buried and top perovskite surface of TLP films after post-treatment of PEDOT:PSS and perovskite by EDDA, respectively. d) XPS spectra of C 1s for PEDOT:PSS and PEDOT:PSS w/ EDDA thin films.

matrix, (ii) form top-interface molecular bridge (ionic bond) and (iii) deprotonation of PSSH to generate PSS^- within the HTL. The proposed mechanisms are suggested as being depicted in Figure 1b and Figure S2. DMSO was selected as the solvent for EDDA to post-treatment of PEDOT:PSS owing to its high dielectric constant and excellent dissolution capacity for both polar and non-polar compounds [26]. EDDA concentration was optimized to 3mg/mL, as shown in Figure S3. As a strong polar aprotic solvent, DMSO forms robust hydrogen bonds with the $-\text{SO}_3\text{H}$ moieties of PSS, as shown in Figure S2 [22]. Upon thermal annealing inside a glovebox, rapid evaporation of DMSO accelerates the removal of excess PSS, thereby allowing EDDA molecules to penetrate and localize within the PSS-rich surface region of PEDOT:PSS. This incorporation facilitates subsequent interfacial interactions with the underlying PEDOT:PSS layer. Owing to its two terminal ammonium groups, EDDA could function as a bifunctional ionic bridge, simultaneously interacting with PSS^- species in PEDOT:PSS and halide ions in the perovskite layer, as shown in Figure 1c. Meanwhile, Ac^- anions exhibit multiple beneficial effects at both interfaces. On the PEDOT:PSS surface, Ac^- facilitates the deprotonation of PSSH into PSS^- , thereby reducing surface acidity and strengthening EDDA anchoring via ionic bond [14, 15]. At the perovskite interface, Ac^- anions can coordinate with undercoordinated $\text{Sn}^{2+}/\text{Pb}^{2+}$ cations and occupy halide vacancies, thereby modulating crystallization kinetics and suppressing defect formation, as illustrated in Figure 1c [27]. Collectively, these synergistic effects highlight the effectiveness of Ac^- -based chelating salts for the simultaneous regulation of PEDOT:PSS surface chemistry and perovskite crystallization behavior, ultimately strengthening interfacial interactions and improving perovskite film quality [15, 28].

To examine the proposed interfacial modification mechanism and to gain a more precise understanding of the surface chemical status of PEDOT:PSS, we performed high-resolution X-ray photoelectron spectroscopy (XPS). The elemental spectra of N 1s, C 1s, S 2p, and O 1s were analyzed for PEDOT:PSS and PEDOT:PSS w/EDDA films. As shown in the N 1s spectra (Figure S4), the PEDOT:PSS w/ EDDA film exhibits a pronounced increase in peak intensity compared with pristine PEDOT:PSS, which is attributed to the higher nitrogen content introduced by EDDA [28]. This finding confirms the successful incorporation of EDDA at the PEDOT:PSS surface and indicates effective anchoring of the protonated $-\text{NH}_3^+$ group onto the PEDOT:PSS [26]. Figure 1d illustrates the deconvoluted C 1s spectrum for PEDOT:PSS and PEDOT:PSS w/EDDA film. The characteristic peaks located at 284.68, 285.88, and 286.84 eV correspond to C—C, C—N, and C—S bonding environments, respectively. Notably, an additional peak at 291.10 eV, associated with the O—C=O moiety originating from Ac^- groups, is observed in the PEDOT:PSS w/EDDA HTL film. This feature provides direct evidence for the incorporation of EDDA-derived $-\text{COO}^-$ group into the post-treated PEDOT:PSS HTL film [23]. In the S 2p region (Figure 2a,b), signals at 163–167 eV and 167–172 eV correspond to S—C bonding in PEDOT and S—O bonding in PSS, respectively [29]. All four characteristic peaks in the PEDOT:PSS w/EDDA film exhibit a shift toward lower binding energy, suggesting that EDDA may reduce the electrostatic interaction (called Coulomb attraction) between PEDOT and PSS. This effect facilitates partial removal of PSS from the film surface [30]. The comparison of PEDOT:PSS w/EDDA film with PEDOT:PSS film revealed a change in S 2p intensity within the

PSS-rich domain, while a significant increase was observed in the intensity associated with the PEDOT-rich domain. This suggests that post-treatment on PEDOT:PSS remove the PSS-rich domain from the surface, thereby exposing the conductive PEDOT-rich domain which will boost the conductivity of PEDOT:PSS. The XPS analysis of the O 1s orbital reveals two peaks at 533.31 and 531.95 eV for the PEDOT:PSS film, which corresponds to oxygen atoms in PEDOT and PSS, respectively, as shown in Figure S5. Upon EDDA surface treatment, both peaks shift to lower binding energies, an effect attributed to EDDA mediated conversion of acidic $-\text{SO}_3\text{H}$ to its anionic form $-\text{SO}_3^-$, indicating a significant change in the surrounding chemical coordination [31, 32]. This evidence supported the hypothesis and treatment mechanism in Figure 1b and Figure S2.

Efficient hole transport in PSCs is intrinsically governed by the electrical conductivity of HTL. However, the presence of excess insulating PSS chains significantly reduces the electrical conductivity of PEDOT:PSS [33, 34]. Moreover, the random distribution of PEDOT and PSS domains in PEDOT:PSS further impedes effective charge transportation. To evaluate the influence of EDDA post-treatment on the conductivity of PEDOT:PSS, a simplified device structure (FTO/HTL/Ag) was fabricated and systematically investigated [35]. The direct conductivity test was performed using current-voltage (I - V) in dark, and conductivity was calculated using the following Equation (1)

$$\sigma = \frac{Id}{AV} \quad (1)$$

Here, I is the current, d is the thickness of HTL (20 nm), A is the active area (0.09 cm^2), and V is the applied voltage. The EDDA modification of the PEDOT:PSS HTL led to a notable increase in its electrical conductivity from 3.12×10^{-3} to $3.86 \times 10^{-3} \text{ mS cm}^{-1}$. This enhancement is attributed to the partial removal of excess PSS chains and the deprotonation of PSSH to PSS^- induced by the EDDA post-treatment, as shown in Figure S6. The enhanced conductivity facilitates more efficient hole extraction and transfer to the external circuit, thereby contributing to the overall improvement in the performance of the PSCs.

To clarify the mechanism behind the observed conductivity enhancement, it is essential to analyze the molecular structure of PEDOT:PSS. Spin-coated PEDOT:PSS films generally comprise a conductive PEDOT-dominant phase and an insulating PSS-dominant phase [36]. Within these domains, PEDOT-dominant regions contain PEDOT^+ and PSS^- chains, while the PSS-dominant regions are dominated by non-ionic PSSH chains [37]. Previous research suggest that charge transport occurs through hopping or tunneling between PEDOT-rich domains, and conductivity can be improved by reducing the proportion of PSSH chains [38]. Upon EDDA post-treatment of PEDOT:PSS film, the $-\text{S=O}$ moiety of DMSO and the protonated amine ($-\text{NH}_3^+$) group of EDDA could form hydrogen bond with $-\text{SO}_3\text{H}$ moieties in PSSH, as shown in Figure S2. Most importantly, Ac^- anions promote the deprotonation of PSSH to PSS^- at the PEDOT:PSS top surface, thereby reducing surface acidity and facilitating the strong ionic coordination between PEDOT:PSS and EDDA through ionic bonding (Figure 1b). This proton exchange reaction, detailed in Equation (2), lowers the acidity of the PEDOT:PSS matrix. The increased content of $-\text{SO}_3^-$

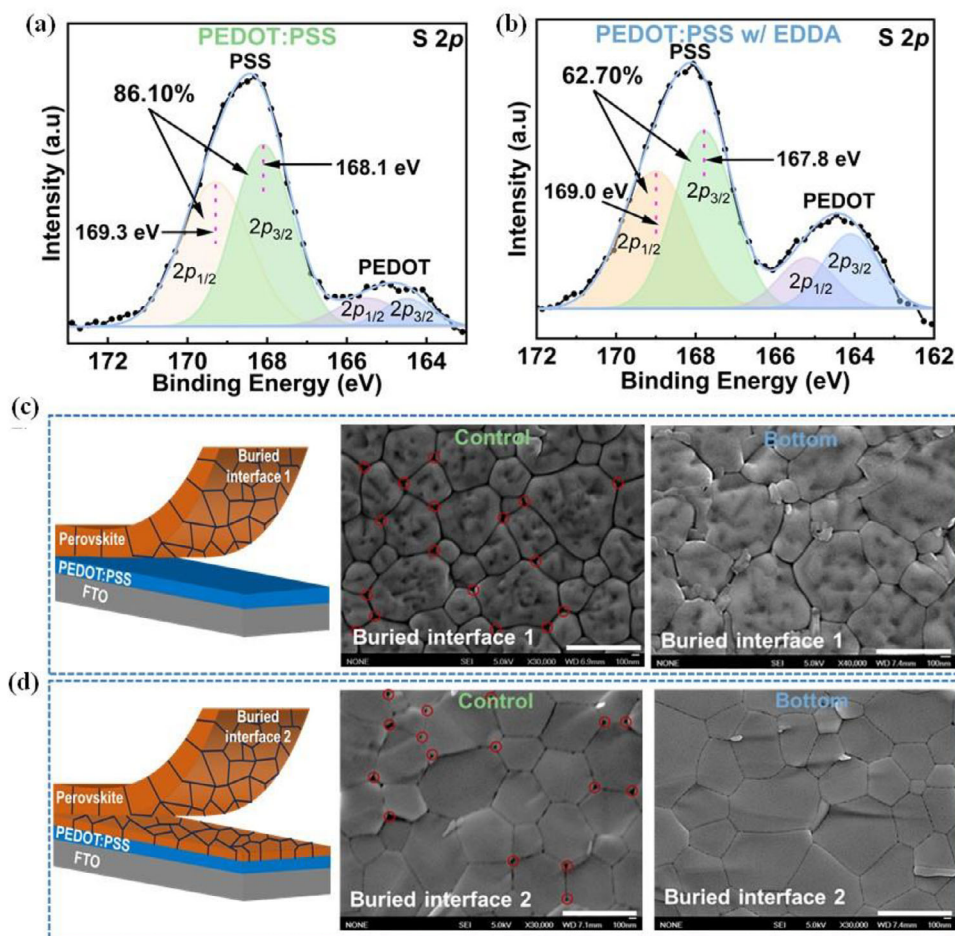
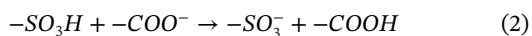


FIGURE 2 | The XPS spectra of S 2p for a) PEDOT:PSS and b) PEDOT:PSS w/ EDDA thin films. c, d) SEM images of buried interfaces of TLP films deposited on PEDOT:PSS and PEDOT:PSS w/EDDA HTL. SEM scale bar:1 μm .

groups play a key role in conductivity enhancement by facilitating better connectivity between PEDOT^+ and PSS^- through $-\text{SO}_3^-$ bridging. [32]



In inverted PSCs, the surface wettability, structural morphology, and photoelectrical properties of HTL strongly influence the crystallization behavior of the perovskite layer, the density of interface defects, and the efficiency of charge injection and transport [39]. The transmittance spectra of the PEDOT:PSS and PEDOT:PSS w/EDDA HTL is shown in Figure S7. The spectrum of the PEDOT:PSS w/EDDA HTL is closely matches that of the PEDOT:PSS HTL, indicating that EDDA effectively prevents parasitic light absorption and improves light transmission rate within the 350–400 nm region. The atomic force microscopy (AFM) was utilized to analyze the surface microstructure of PEDOT:PSS on FTO substrates, as shown in Figure S8a,b. The root-mean-square (RMS) roughness of PEDOT:PSS w/EDDA film (RMS = 19.7 nm) is lower than that of the PEDOT:PSS film (RMS = 23.6 nm), indicating that EDDA post-treatment is not only disperses on PEDOT:PSS but also polished the surface of PEDOT:PSS. The AFM lines profiles confirmed the surface roughness reduction using EDDA-DMSO surface treatment, as shown in Figure S8c. The RMS roughness of PEDOT:PSS w/EDDA film is reduced

due to the solvent-induced surface relaxation. A smoother HTL promotes the wettability of perovskite precursor solution on the surface and minimizes localized solvent trapping during film formation. Beyond the morphological effect, EDDA molecules coordination with ionic species in perovskite precursor, as illustrated in Figure 1c and actively modulate the perovskite nucleation density and perovskite crystallization. The synergistic combination of improved interfacial smoothness and EDDA-induced coordination chemistry promotes uniform nucleation and controlled grain growth, resulting in perovskite films with higher crystallinity and reduced microstructural disorder. Direct experimental evidence supporting the chemical coordination between EDDA and perovskite ions is provided in the subsequent sections. Additionally, the surface potential (SP) distribution was utilized using Kelvin probe force microscope (KPFM), as shown in Figure S8d,e. The PEDOT:PSS w/EDDA films demonstrate a significant higher SP_{mean} of 23.3 mV compared to 15.5 mV for PEDOT:PSS film, indicating that a more p-type surface is achieved through EDDA post-treatment of PEDOT:PSS [40]. The KPFM maps show no direct spatial correlation with AFM topography, indicating that the observed surface-potential variations are not dominated by morphological features. Instead, the potential changes are attributed to chemical modification of PEDOT:PSS induced by EDDA-DMSO post-treatment. More importantly, the difference of surface potential changes the work

function and turned the highest occupied molecular orbital (HOMO) level that helps to enhance efficient charge transportation [32, 41]. The surface properties of the HTL strongly influence the crystallization behavior of the overlying perovskite layer. To elucidate the role of the buried interface in governing perovskite film growth, the buried interfacial region was investigated by scanning electron microscopy (SEM). The buried interfacial region was exposed via a peel-off technique using a UV-curable adhesive. The adhesive was applied to the top surface of the perovskite film, followed by a clean FTO substrate was placed on it. Upon UV exposure, the adhesive was cured, and the adhered layers were gently peeled off, leading to peel-off of the perovskite film from the FTO/HTL. This peel-off process reveals two distinct interfacial surfaces of the TLP films, hereafter referred to as “buried interface 1” and “buried interface 2”, as shown in Figure 2c,d. For the Control perovskite, the exposed buried interface 1 displayed clearly defined grain boundaries and quite small perovskite grains. The observed morphology suggests that the perovskite layer separated easily because of the inherently weak interfacial bonding between the acidic, PSS-rich PEDOT:PSS surface and the TLP layer. The high density of sulfonate groups and strong surface acidity of PEDOT:PSS interface promotes non-uniform nucleation at the HTL/perovskite interface, leading to inadequate interfacial adhesion and initiating heterogeneous crystal growth. As a result, small and irregularly distributed grains are observed at the buried interface 1 of the Control film, indicating uncontrolled crystallization dynamics during the early stages of perovskite formation. In contrast, PEDOT:PSS post-treated with EDDA displayed a markedly different buried interfacial morphology. After peeling off the perovskite layer from the FTO/HTL substrate, the few grain boundaries were obscured by conformal coverage and the characteristic FTO footprint is not clearly visible. This morphological observation indicates incomplete delamination of the perovskite layer from HTL, arising from enhanced interfacial adhesion induced by EDDA–DMSO modification of PEDOT:PSS. As a result, perovskite films deposited on EDDA-modified PEDOT:PSS exhibit larger and more uniform grains at Buried interface 1. A similar morphological evolution is observed at buried interface 2, where EDDA-modified TLP films showed higher grain compared to Control TLP films, as shown in Figure 2c,d. Most importantly, the Control TLP film at buried interface 2 showed many pinholes between grain boundaries, indicative of uncontrolled nucleation and incomplete grain coalescence. In contrast, the Bottom TLP at buried interface 2 showed uniform crystal grain with few pinhole-like features. Those pinholes may appear due to stress during the peel-off process of perovskite layer from HTL. Collectively, these observations confirm that EDDA treatment fundamentally alters the interfacial chemistry and crystallization dynamics of TLP. By strengthening interfacial adhesion, modulating surface energy, and coordinating with interfacial metal ions, EDDA guides crystal growth from the bottom upward, yielding a more uniform buried interface.

Building on the above evidence, EDDA is confirmed to form a binding bridge with PEDOT:PSS HTL, which subsequently coordinates with the perovskite lattice during film deposition, as shown in Figure 1c and Figure 2c,d. It is well known that crystallization of Sn-based perovskite is faster than Pb-based perovskite [13, 18, 42]. The EDDA molecule contains two electron-rich functional groups (Ac^-) and two versatile functional groups

($-\text{NH}_3^+$) [43]. These functional groups of EDDA cooperatively regulate nucleation and growth kinetics. Furthermore, EDDA post-treatment of perovskite top surface effectively passivates surface defects, leading to a high-quality perovskite layer. To directly verify the coordination interaction between EDDA and $\text{SnI}_2/\text{PbI}_2$, a liquid-state photon nuclear magnetic resonance (^1H NMR) analysis was performed. Figure 3a shown the ^1H NMR spectra of EDDA, EDDA + PbI_2 and EDDA + SnI_2 in a solution of deuterated *N,N*-dimethylformamide- d_6 ($\text{DMSO-}d_6$). The $-\text{CH}_2$ protons of EDDA, initially resonating at $\delta = 2.65$ ppm, exhibited a downfield (to a higher ppm value) shift for both metal complex, indicative of protonation at the adjacent $-\text{NH}_2$ group [44]. The resonance peak corresponding to the $-\text{NH}_3^+$ protons appeared at $\delta = 6.82$ ppm. This peak shifted to higher ppm value (downfield) due to the Lewis acid-base interaction with PbI_2 and SnI_2 . The Ac^- group near $-\text{NH}_3^+$ group in EDDA coordinates to metal cation like Pb^{2+} or Sn^{2+} , donating electron density via its oxygen lone pair to metal ions. This electron donation from oxygen of Ac^- group reduces the electron density of it and nearby $-\text{NH}_3^+$ group. As a result, the $-\text{NH}_3^+$ protons become more deshielded and corresponding peak shift to higher ppm value. Interestingly, the peak shift is higher for SnI_2 due to the stronger coordination between Ac^- group and SnI_2 than PbI_2 . The interaction of $\text{C}=\text{O}$ in EDDA with $\text{Sn}^{2+}/\text{Pb}^{2+}$ was additionally confirmed through fourier transform infrared spectroscopy (FTIR) measurements. The $\text{C}=\text{O}$ stretching vibration peak at 1640 cm^{-1} shifts to a lower wavenumber following mix with $\text{SnI}_2/\text{PbI}_2$. This shift suggests the formation of chelate complex via $\text{COO}^- (\text{C}=\text{O}-\text{Sn})/\text{COO}^- (\text{C}=\text{O}-\text{Pb})$ [45, 46]. The more prominent shift observed in the EDDA + SnI_2 adduct compared to EDDA+ PbI_2 adduct suggests a more robust interaction between EDDA and Sn^{2+} ions than with Pb^{2+} ions, as shown in Figure 3b(Left) [47, 48]. The robust interaction due to the O atoms of EDDA donate electrons to Sn^{2+} ions more easily than Pb^{2+} ions and weakens the $\text{C}=\text{O}$ bond. In addition, the two signals appear at around 1550 and 1227 cm^{-1} for EDDA + SnI_2 adducts, as shown in Figure 3b(Right). The strong absorption signal at around 1550 cm^{-1} can be assigned with the amide II region, which involves $\text{C}-\text{N}-\text{H}$ in-plane bending and out-of-phase $\text{C}-\text{N}$ stretching vibrations. The absorption band at around 1271 cm^{-1} is linked to the amide III region, resulting from the in-plane $\text{C}-\text{N}-\text{H}$ stretching coupled with in-phase $\text{C}-\text{N}$ stretching [49, 50]. The EDDA + PbI_2 adducts follows the same trend as EDDA + SnI_2 . The absorption signal at 1543 and 1265 cm^{-1} can be assigned with the amide II region and the amide III region, respectfully. The findings clearly indicate that amide formation in the EDDA + SnI_2 and EDDA + PbI_2 adducts, likely resulting from a reaction between Ac^- group and $-\text{NH}_3^+$ group of EDDA with SnI_2 and PbI_2 .

To elucidate the interaction between EDDA and main A-site component formamidinium (FA) cation, the ^1H NMR analysis was carried out. Figure 3c displays the ^1H NMR spectra of EDDA, formamidinium iodide (FAI), and their mixture (EDDA + FAI). The peaks at 2.48 ppm corresponds to residual $\text{DMSO-}d_6$. In the mixed EDDA + FAI spectrum, the $-\text{CH}_2$ peak of EDDA at 2.65 ppm exhibited a downfield shift and a new peak appears at 3.52 ppm, which is likely attributed to $-\text{CH}_2$ groups adjacent to a protonated nitrogen (N^+H_2), thereby confirming the protonation of EDDA. The $-\text{NH}$ peaks of FA^+ at 7.83 and 7.78 ppm, and $-\text{NH}$ peak of EDDA at 6.81 ppm merged or shifted to 7.69 and 7.76 ppm, indicating modifications in hydrogen bonding or exchange

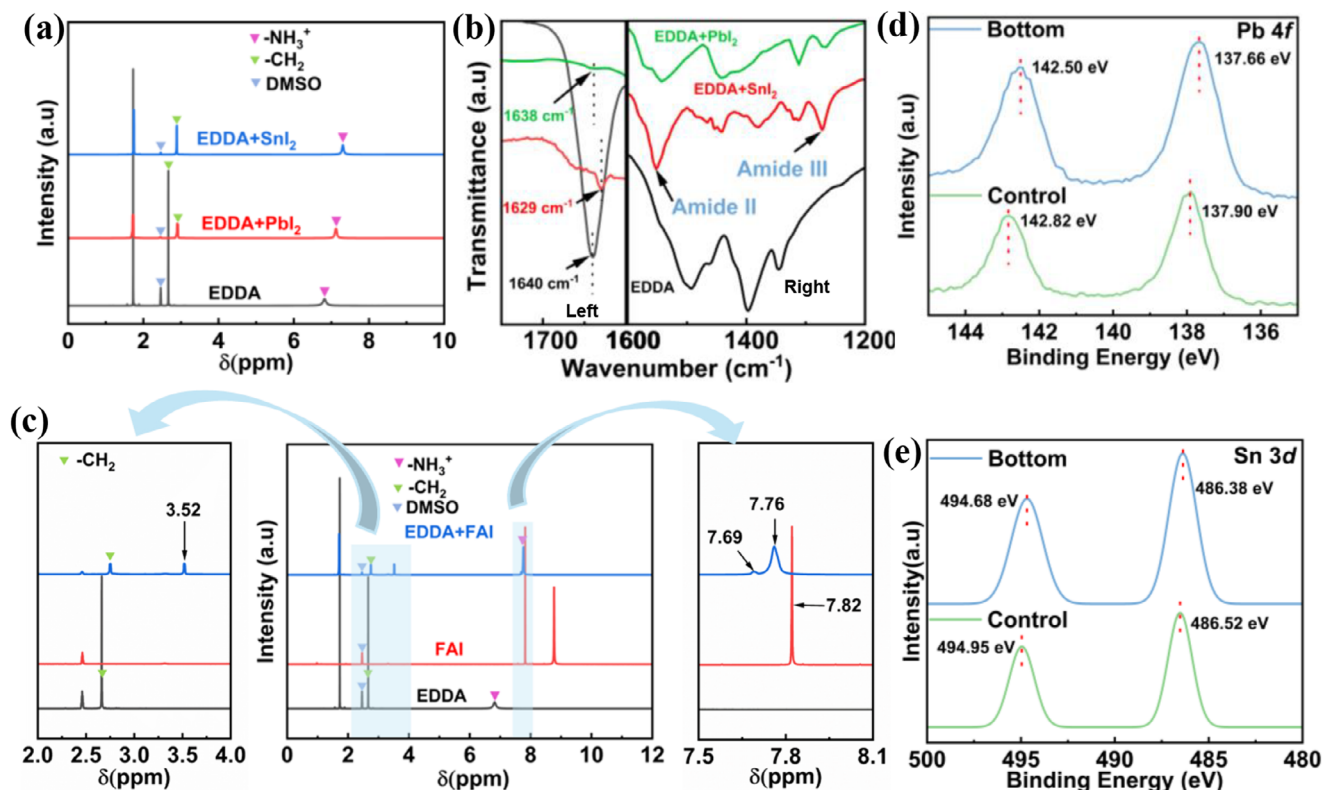


FIGURE 3 | a) ^1H NMR Spectroscopy of EDDA, EDDA + PbI_2 , and EDDA + SnI_2 . b) FTIR spectrum of EDDA adduct, EDDA + SnI_2 adduct and EDDA + PbI_2 adduct. c) ^1H NMR Spectroscopy of EDDA, FAI, and EDDA + FAI. XPS spectra of d) Pb 4f and e) Sn 3d for Control and Bottom perovskite film.

environments. The $-\text{CH}_3$ peak at 1.8 ppm is invariant, suggesting no structural change at that site. This chemical shift indicates that EDDA accepts a proton from the acidic FAI, resulting in the formation of a new ion-pair or hydrogen-bonded complex.

XPS analysis provides further compelling evidence for the chemical interaction and coordination bonding between EDDA and the metal halide components ($\text{PbI}_2/\text{SnI}_2$) within the perovskite lattice. Figure 3d,e illustrates that the core-level spectra of Pb 4f and Sn 3d for the EDDA-modified (Bottom) perovskite film displayed significant shifts toward lower binding energies in comparison to those of the Control perovskite film. Specifically, the Pb 4f $_{7/2}$ and Pb 4f $_{5/2}$ peaks exhibited shifts from 137.98 and 142.85 eV to 137.65 and 142.55 eV, respectively. Similarly, the Sn 3d $_{5/2}$ and 3d $_{3/2}$ peaks moved from 486.52 and 494.95 eV to 486.38 and 494.68 eV, respectively. These systematic downshifts indicate an increase in the local electron density around the Pb^{2+} and Sn^{2+} ions, consistent with electron donation from the lone electron pairs of the oxygen atoms of the $\text{C}=\text{O}$ groups to the unoccupied 6p orbitals of Pb^{2+} and the unoccupied 5p orbitals of Sn^{2+} . Such chelating coordination interactions effectively stabilize the metal-halide framework, reduce the reactivity of undercoordinated metal sites, and moderate the nucleation density during perovskite film formation. Such modulation leads to control and homogeneous nucleation and format high quality perovskite films with reduced defects densities.

To understand more deeply the effect of buried interface on crystallization dynamic of TLP, we systematically investigated

the surface morphology evolution and phase progression during thermal annealing of TLP films. SEM measurements were utilized to track the morphological evaluation of perovskite thin films annealed at 70°C for different durations of time, as presented in Figure 4a. The time-dependent SEM observations reveal a crystallization pathway involving the transformation from an intermediate phase to the perovskite phase, evidenced by gradually enlarging the grain size [51–54]. For the Control TLP film, uncontrolled nucleation at the buried interface and uneven growth rates accelerated the highly inhomogeneous crystallization, manifested by coexist larger crystal, smaller crystal and pinholes. Notably, the coexistence of large and very small crystals even at prolonged annealing times suggests continuous late-stage nucleation, incomplete grain coalescence, or inhibited boundary migration. In contrast, EDDA modification at buried interface fundamentally alters the perovskite crystallization behavior. The strong coordination interactions between EDDA and interfacial metal ions effectively regulate both the nucleation density and nucleation sites, resulting in more homogeneous nucleation and crystal growth. As a result, the final TLP film shows larger grain sizes with substantially reduced small crystallites, highlighting a marked improvement in film uniformity and structural quality compared with Control TLP films. To correlate morphological progression with crystallographic phase transition, X-ray diffraction (XRD) measurements were performed on perovskite films annealed for various durations, as shown in Figure 4b,c. With increase the annealing time, the diffraction peak intensity of (100) and (200) planes are gradually increase for both samples, accompanied by

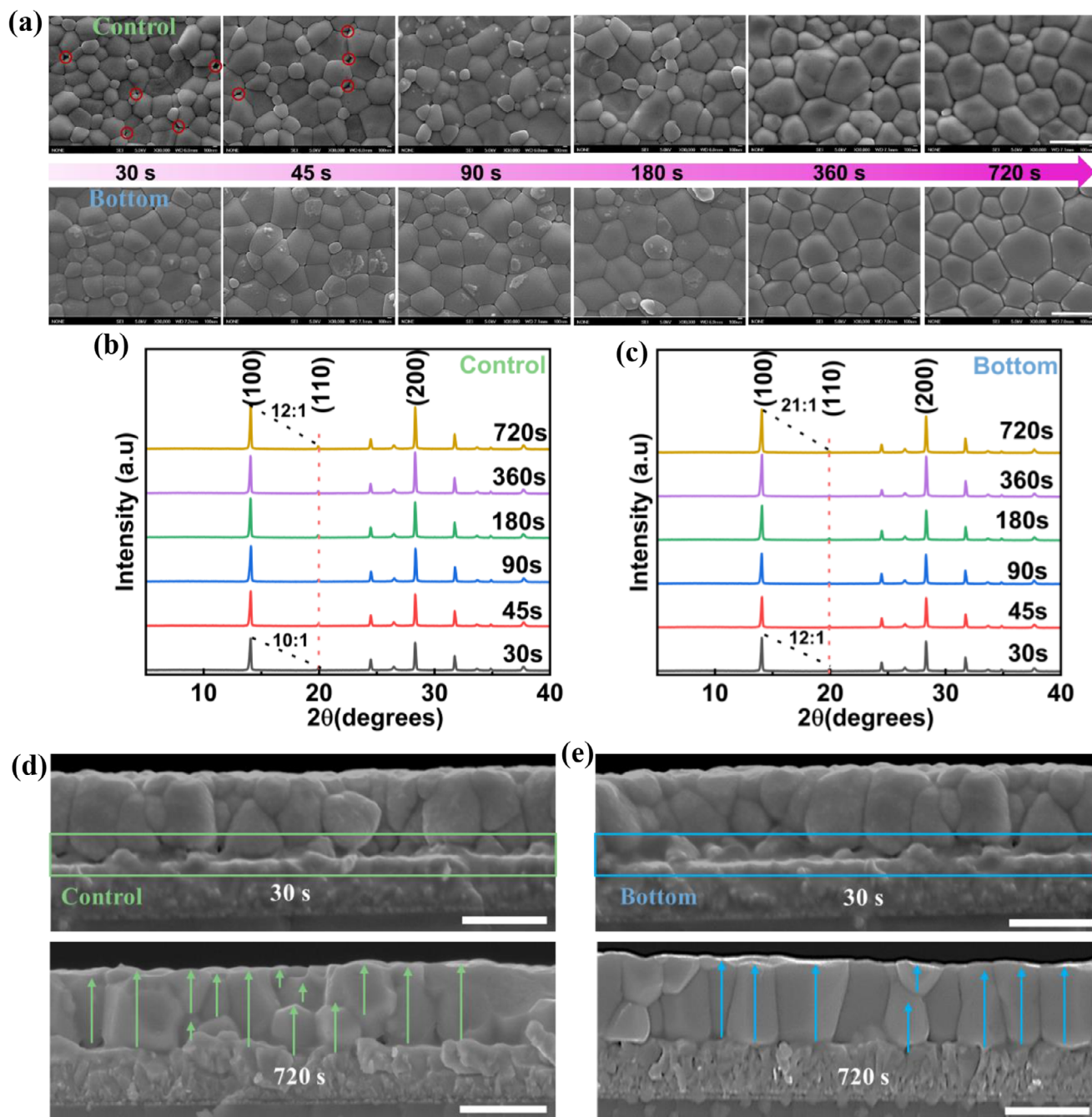


FIGURE 4 | a) SEM images, b, c) XRD patterns, and d, e) Cross-sectional SEM images of TLP films deposited on PEDOT:PSS and PEDOT:PSS w/ EDDA for different annealing times and annealed at 70°C inside glovebox. scale bar:1 μ m.

the systematic enhancement in the (100)/(110) peak intensity ratio. This finding reveals the crystalline enhancement and preferential orientation along the (100) plane for both TLP films [55, 56]. For Control TLP films deposited on PEDOT:PSS, the peak (100)/(110) intensity ratio increases slightly from ~10:1 at 30 s to ~12:1 at 720 s, indicating slow and incomplete orientation where both (100) and (110) planes are coexisted. This weak orientation selectivity is fully consistent with SEM observations showing mixed grain sizes, suggesting random nucleation behavior. In contrast, the perovskite films grown on PEDOT:PSS w/EDDA show a much stronger preferential orientation, with the (100)/(110) intensity ratio sharply increas-

ing from ~12:1 at 30 s to ~21:1 at 720 s. This pronounced enhancement of (100)-oriented diffraction peak, together with the suppression of (110) reflections, correlates well with the formation of large, uniform grains observed in SEM images (Figure 4a; Figure S9). These result indicates that EDDA modification of buried interface promotes (100)-facet orientation [16, 55]. The (100)-facet orientation has likely arisen from the interaction between amine and carboxylate groups of EDDA and the perovskite precursor ions, which modulates the interfacial perovskite crystallization and stabilizes the intermediate phase, guiding the crystal growth along the (100) plane direction. This interfacial regulation accelerates oriented grain coalescence,

minimizes (110)-oriented domains, and enhances overall film quality.

This crystallization trend is further confirmed by cross-sectional SEM observations, as shown in Figure 4d,e, which provide direct insight into the vertical growth behavior of the TLP films. At the early annealing stage (30 s at 70°C), the Control TLP layer displayed a high density of small grains with irregular vertical alignment, numerous grain boundaries, and pronounced voids at HTL/perovskite buried interface, consistent with rapid and uncontrolled nucleation. The presence of these interfacial voids indicates weak adhesion and poor interfacial contact between the PEDOT:PSS HTL and the perovskite layer, which can hinder efficient charge extraction and promote interfacial recombination in the PSC structure. In contrast, the perovskite film deposited on PEDOT:PSS w/EDDA displays significantly larger grains at this early crystallization stage, suggesting that the functional groups of EDDA effectively coordinated with the perovskite precursor ions at the buried interface. This coordination moderate's nucleation behavior and promotes more uniform and vertically oriented crystal growth. Upon extending the annealing time to 720 s, the Control films continue to exhibit a heterogeneous microstructure comprising a mixture of small and large grains, suggesting persistence of random nucleation and incomplete grain coalescence. Conversely, the Bottom TLP films evolve into dense and compact microstructures demonstrated by mostly vertical grain alignment and substantially increased grain sizes, with only a few small crystallites remaining. This distinct morphological evolution indicates the critical role of EDDA-modified buried interface enhances interfacial adhesion and regulates vertical crystal growth. By suppressing uncontrolled nucleation and facilitating coherent grain propagation across the film thickness, EDDA treatment yields perovskite layers with improved structural integrity and superior film quality. This improvement leads to enhance charge transportation and reduce recombination in TLP solar cells.

To further evaluate the effect of EDDA post-treatment on the crystallinity and surface quality of perovskite films fabricated on PEDOT:PSS w/ EDDA, XRD analysis was used. As shown in Figure S10, all Control, Bottom and Target TLP films exhibit diffraction patterns characteristic of a single-phase 3D perovskite structure, with no evidence of 2D perovskite formation or impurity phases. Importantly, neither the modification of PEDOT:PSS nor the EDDA post-treatment of the TLP layer induces additional diffraction peaks associated with low-dimensional perovskite formation. Notably, the Target TLP films show enhanced crystallinity, as evidenced by a reduced full width at half maximum (FWHM) value, as shown in Table S1. This resulted indicating improved crystalline coherence and reduced lattice disorder. These results confirm that EDDA treatment promotes crystal quality without altering the intrinsic perovskite phase. In addition, the surface morphology and grain size of perovskite films were investigated by SEM. As depicted in Figure 5a–c, the Bottom TLP films exhibit enlarged grain sizes compared with the Control films, consistent with buried interface regulated crystallization. A significant surface refinement was noted in the EDDA post-treated perovskite film called Target, likely attributable to the removal of loosely attached upper layers of the perovskite layer called chemical polishing [57, 58]. In contrast, Control films displayed discrete features, likely attributed to SnF₂ residues,

situated at the grain boundaries. Those residues are likely reduced after post-treatment by EDDA, indicating effective surface cleaning and defect mitigation. The chemical polishing effect was confirmed by AFM analysis, as shown in Figure 5d,e. The R_q decreased from 30.2 nm for the Control TLP to 22.2 nm for Target TLP film, indicating enhanced surface homogeneity. The analysis of AFM line scans indicates that the height difference between grain interiors (GI) and grain boundaries (GB) in the Target film is significantly diminished when compared to Control films, as shown in Figure 5f. The results confirmed that EDDA post-treatment reduced SnF₂ residues on the surface and polished the perovskite top surface. Consistent with these structural improvements, the KPFM measurements (Figure S11) demonstrate a markedly reduced potential contrast between GIs and GBs in the Target TLP film compared to the Control TLP film. This observation suggests that the Control film likely has a deeper Fermi level at the GBs, attributed to the increased defect densities. Self-p-doping with Control TLP films resulted in an increase in defect densities at the perovskite surface. The EDDA post-treatment of TLP reduced the surface defects at the grain boundaries by ionic and coordination bonding. To quantitatively assess defect suppression, we examined the oxidation state of Sn presented on the film surface by XPS. The Sn 3d_{5/2} peaks were divided into two separate peaks, corresponding to Sn²⁺ and Sn⁴⁺, as shown in Figure 5g,h. The Target film showed the lower Sn⁴⁺ content, indicating lower oxidation of Sn²⁺ due to the passivation of EDDA. The passivation effect is also verified by XPS full spectrum of Sn 3d and I 3d for control and Target TLP film. Our observations indicated that the metal cation (Sn²⁺) peaks of Target TLP exhibited shifts toward lower binding energies compared to the Control TLP film, as shown in Figure S12. This finding agreed with the interaction between perovskite and —C=O, and —NH₃ functional groups present in EDDA. Similarly, the I 3d_{3/2} and I 3d_{5/2} peaks, initially located at 630.36 and 618.91 eV in the Control TLP film, exhibit a binding energy downshift to undergo a shift toward 630.16 and 618.63 eV in the Target TLP film, as shown in Figure S13. Moreover, the slight energy shift suggests that EDDA effectively passivate the I[−] ions vacancy defect and inhabit the I[−] ions migration of perovskite. This shift is attributed to ionic interactions and interfacial hydrogen bonding between —NH₃⁺ groups and iodide (I[−]) ions coordinated the [PbI₆]^{4−}/[SnI₆]^{4−} octahedral framework.

To evaluate the impact of the chelating molecular bridge on perovskite film quality, Steady-state photoluminescence (PL) spectroscopy was employed. The perovskite films were deposited on the Glass/HTL substrate. Upon irradiation from the bottom side, the Bottom perovskite film exhibits an increased PL intensity relative to the Control perovskite film (Figure 5i). This observation indicates a reduction in nonradiative recombination sites and an improvement in perovskite film quality at the buried interface, aligning with prior research findings [59, 44]. The effect of EDDA post-treatment on the perovskite top surface was further evaluated by PL measurements. The Target perovskite film shows an additional increase in PL intensity compared with the Bottom film, confirming further suppression of nonradiative recombination following surface treatment. This improvement is attributed to EDDA-induced passivation of surface defect states, including undercoordinated metal ions and halide vacancies, thereby yielding a perovskite layer with reduced trap-assisted recombination.

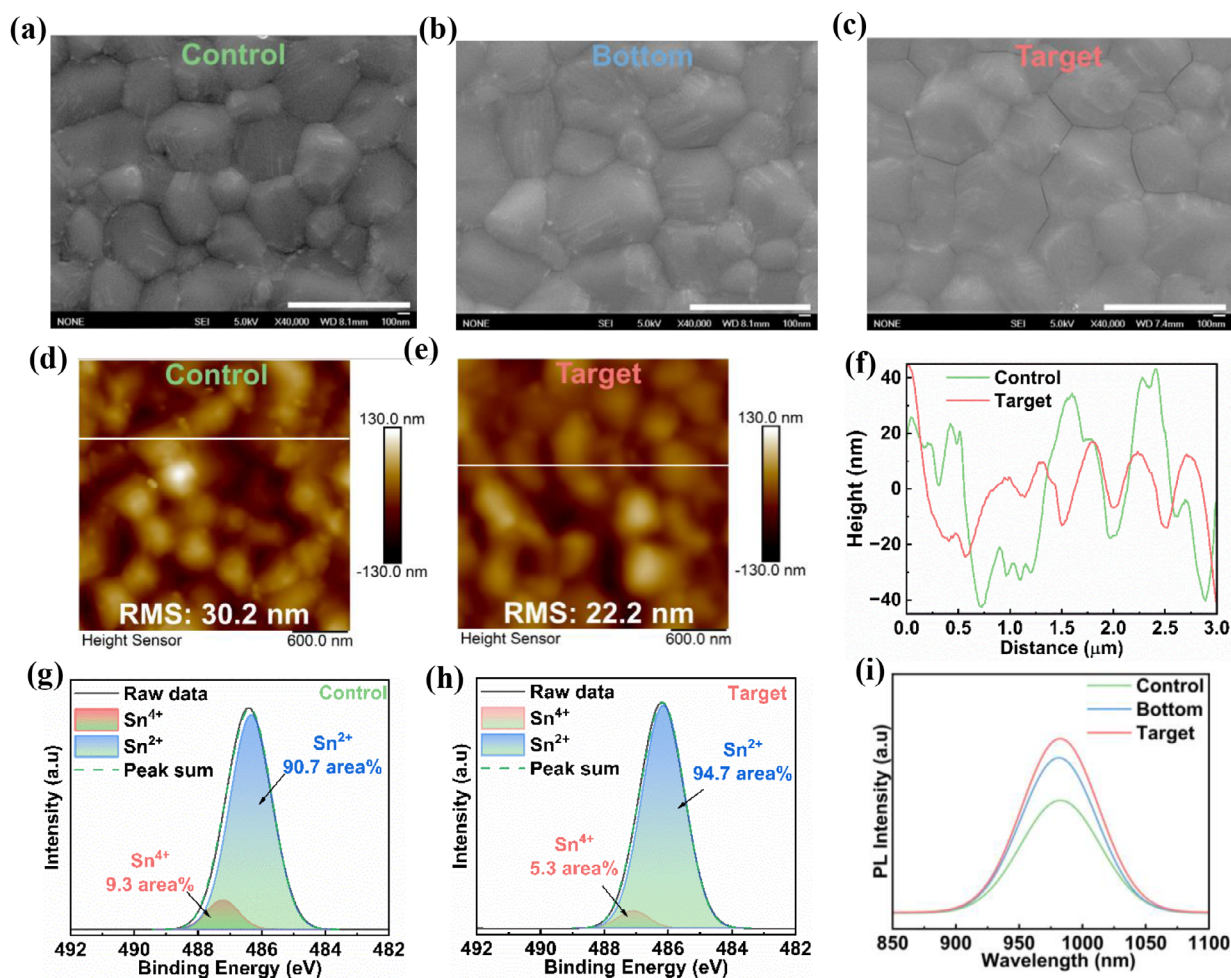


FIGURE 5 | Top-view SEM images of a) Control, b) Bottom and c) Target TLP film. SEM scale bar: 1 μm . AFM images of d) Control and e) Target TLP films. f) Corresponding AFM line scans of Control and Target TLP films. Sn $3d_{5/2}$ XPS spectra of the g) Control and h) Target TLP films. i) Steady-state PL spectra of TLP films.

All prepared perovskite films demonstrate excellent optical characteristics, with strong light absorption range from 300 to 1000 nm, as shown in Figure S14. The absorption edges confirm that the mixed TLP maintains a consistent optical bandgap of approximately 1.27 eV (Figure S14) indicating that neither PEDOT:PSS modification nor EDDA post-treatment perturbs the intrinsic band structure of the absorber. The energy level alignment of the PSCs, depicted in Figure S15 is based on an inverted device configuration with the structure: FTO/PEDOT:PSS (HTL)/perovskite/ C_{60} (ETL)/BCP/Ag. Given the significance of interfacial energetics in governing charge extraction and recombination, the valence band maximum (VBM) values of the HTL and perovskite layers were experimentally determined using an AC-3E photoelectron spectrometer. In addition, the conduction band minimum (CBM) values were calculated from the measured optical bandgap and VBM (Figure S16). Notably, the EDDA treatment effectively suppressed Sn^{2+} oxidation, leading to shallower VBM and CBM position for the perovskite layer. This favorable energetic shift leads to improved band alignment at both the HTL/perovskite and perovskite/ETL interfaces, thereby reducing interfacial energy barriers. As a result, hole and electron extraction and transport are simultaneously facilitated, mini-

mizing carrier accumulation and nonradiative recombination losses.

To evaluate the impact of an EDDA post-treatment at both buried interface and perovskite top surface, inverted TLP solar cells were fabricated with a configuration of FTO/PEDOT:PSS/ $\text{Cs}_{0.1}\text{MA}_{0.3}\text{FA}_{0.6}\text{Pb}_{0.5}\text{Sn}_{0.5}\text{I}_3$ / C_{60} /BCP/Ag, as shown in Figure S17. The current density-voltage (J - V) responses of champion devices, recorded under simulated AM 1.5 G illumination, as shown in Figure 6a. For control devices, the PCE of 20.03% was recorded in the reverse scan, with short circuit current density (J_{SC}) of 31.20 mA cm^{-2} , an open circuit voltage (V_{OC}) of 0.826 V and fill factor (FF) of 77.75%. For Bottom devices, the PCE of 22.04% was recorded in the reverse scan, with J_{SC} of 31.96 mA cm^{-2} , V_{OC} of 0.863 V and fill factor (FF) of 79.92%. The Target champion device with both buried interface and top surface modifications, the PCE of 23.30% was achieved with J_{SC} of 32.48 mA cm^{-2} , V_{OC} of 0.877 V and FF of 81.81%. The external quantum efficiency (EQE) curves for the champion Control, Bottom and Target devices are shown in Figure 6b. The integrated J_{SC} values for the Control, Bottom and Target are 30.97, 31.46, and 31.97 mA cm^{-2} , respectively, demonstrate consistency with experimentally measured J_{SC} derived from J - V curves. The

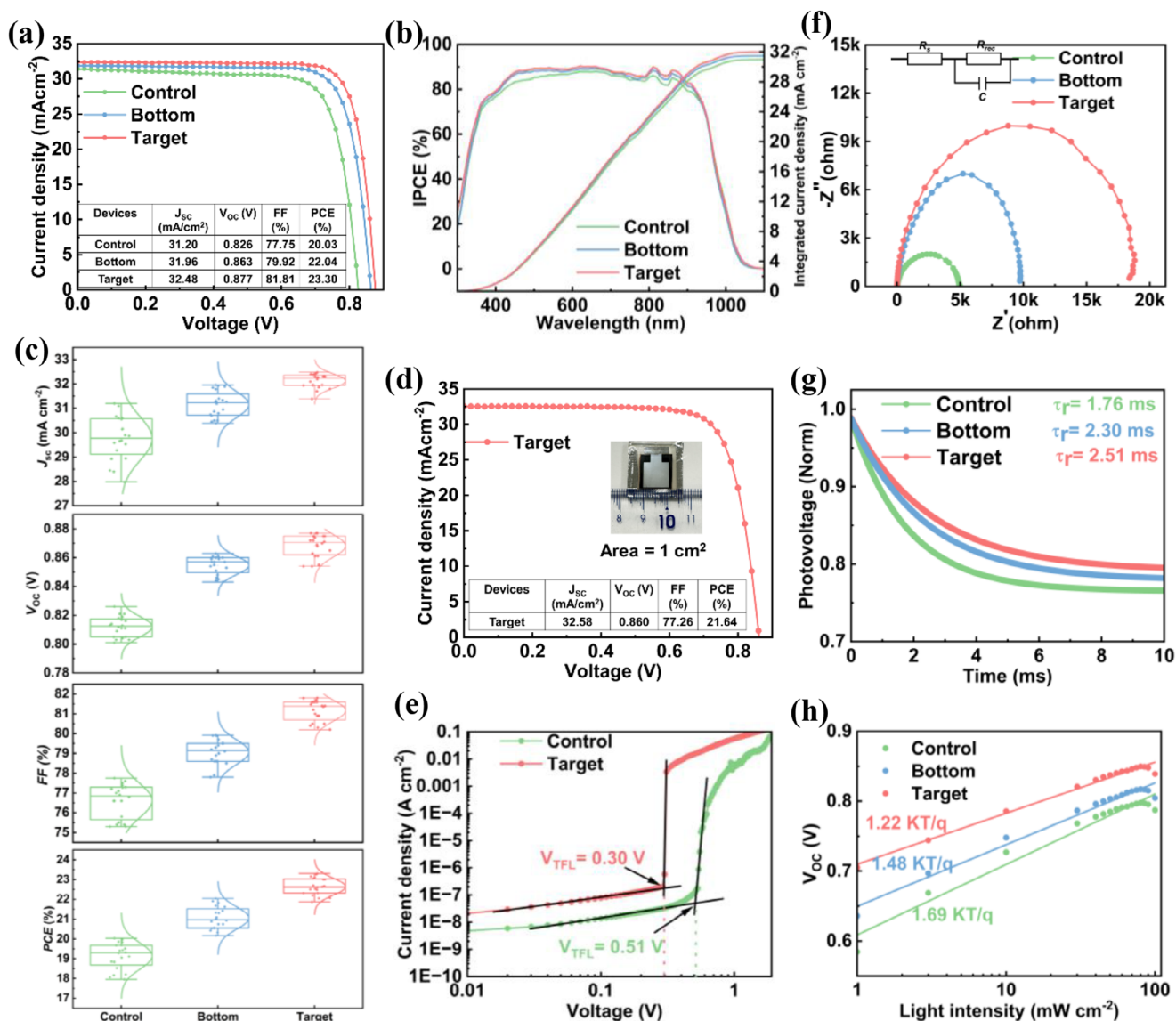


FIGURE 6 | a) Reverse J - V curves of the champion devices. b) IPCE curves of the champion devices. c) Statistical performance parameters distribution of the champion devices. d) Reverse J - V curves for Target champion devices with large active area (1 cm²). e) SCLC measurement for hole-only devices of Control and Target sample. f) EIS, g) TPV, and h) V_{oc} vs light intensity of the TLP devices.

performance improvement of the Target PSC due to the enhanced interfacial connection resulting from chelation effect leads to the formation of more uniform PVKs films and lower surface defects. Figure 6c presents the statistical distribution of key photovoltaic parameters such as J_{sc} , V_{oc} , FF and PCE for both Control, Bottom and Target PSCs. A comparative investigation indicates significant improvements across all performance indicators for the Target devices. Enhanced reproducibility is due to the improvement of film quality and reduced defects densities at the interfaces and boosting the devices' performance. Leveraging the remarkable reproducibility, we fabricated large 1 cm² area PSCs, as illustrated in Figure 6d. The extensive area PSC demonstrates a PCE of 21.64% for Target devices when measured in the reverse scan direction, with J_{sc} , V_{oc} , and FF values recorded at 32.58 mA/cm², 0.860 V, and 0.7726, respectively.

The notable advancements in the device performance mostly emerged from the considerable improvements in V_{oc}

and FF, associated with defect density and carrier recombination (R_{rec}) within the devices. To quantitatively evaluate defect densities in the devices, hole-only devices (FTO/PEDOT:PSS/perovskite/PTAA/Ag) were fabricated and evaluated using Space-charge-limited current (SCLC) measurements. The voltage at which the traps become filled is designated as the trap-filled limit voltage (V_{TFL}), which can be calculated using the subsequent Equation (3):

$$n_{trap} = 2\epsilon\epsilon_0 V_{TFL} / qL^2 \quad (3)$$

where, q is the elementary charge, n_{trap} is trap-state density, L is the thickness of perovskite absorber layer, ϵ is relative dielectric constant of the perovskite materials, ϵ_0 is the vacuum permittivity. Figure 6e illustrates that V_{TFL} of Control device was roughly 0.51 V. The Target device exhibited a significantly lower V_{TFL} of 0.30 V. The results demonstrate a reduction in hole trap-state density from 3.10×10^{14} cm⁻³ for the Control device to 1.82×10^{14} cm⁻³

for the Target samples, signifying suppressed trap densities. This enhancement suggests a reduction in interfacial defect sites and decreased carrier trapping, resulting in improved V_{OC} and FF.

To gain deeper insight into the charge transport and recombination behavior, dark J - V measurements of the PSCs were conducted in dark conditions. As shown in Figure S18, the Target devices displayed a significantly lower dark current density under both negative and positive bias voltages in comparison to the Control device. This suggests enhanced charge extraction, decreases leakage currents in the Target devices. These improvements originate from the effective reduction of trap-state densities at both the buried interface and the perovskite top surface enabled by EDDA chelation and passivation. To further support these observations, electrical impedance spectroscopy (EIS) was utilized to investigate the properties of charge transport and carrier recombination. The Nyquist plots shown in Figure 6f demonstrate a primary semicircle in the low frequencies' region, mainly due to a constant phase element and a R_{rec} . Notably, the Target device displayed a markedly larger semicircle, indicating a substantially higher R_{rec} and a significantly lower recombination rate relative to the Control device. The findings indicate that EDDA modifications at both the buried interface and top perovskite surface significantly reduce carrier recombination in the device, correlating with a decrease in defect density. The carrier dynamics were further investigated by transient photovoltage (TPV) and transient photocurrent (TPC) measurements of the TLP devices. As shown in Figure 6g, the Target devices exhibited a significantly longer TPV decay lifetime of 2.51 ms, compared to 1.76 ms for the Control devices, demonstrating effective suppression of interfacial non-radiative recombination. Moreover, the Target devices displayed a reduced TPC decay time of 687 ns, in contrast to the Control device's 1046 ns, implying enhanced charge carrier extraction and transfer efficiency, as shown in Figure S19.

The ideality factor (n) is a significant parameter for evaluating charge extraction and recombination processes in devices. To determine this value, we measured the J - V curves under different light intensities from 0.01 sun to 1 sun. Figure 6h illustrates that the V_{OC} exhibits a linear relationship with the logarithm of the light intensity, facilitating the extraction of the ideality factor through the standard diode equation:

$$V_{OC} = \frac{nK_B T}{q} \ln \left[\frac{I}{I_0} + 1 \right] \quad (4)$$

where, n is the ideality factor, K_B represents the Boltzmann constant, T denotes the temperature measured in Kelvin, I represent the light intensity and I_0 represents the initial light intensity. Using Equation 4, we calculated the n values for both devices to gain insight into their underlying recombination pathways. An n value greater than 1 generally indicates the presence of trap-assisted Shockley-Read-Hall (SRH) recombination. The Control device demonstrated a n value of 1.69, whereas the Target device presented a notably lower n value of 1.22. The observed decrease in the ideality factor indicates a reduction in trap-mediated recombination in the Target devices. Capacitance-voltage (C - V) measurements were performed to evaluate the built-in potential (V_{bi}) of the devices, as illustrated in Figure S20. The Target device exhibited a V_{bi} of 0.72 V, whereas the Control device displayed

a V_{bi} of 0.66 V. An elevated V_{bi} promotes charge separation, indicating better energy level alignment, and improved interfacial carrier transport, resulting in a higher V_{OC} in the Target devices.

The EDDA modification at buried interface and top perovskite surface may improve the stability of the devices alongside enhancing efficiency. The operational and storage stability of the devices were monitored. Figure 7a presents the stability for encapsulated devices under the maximum power point tracking (MPPT) in an ambient environment under one sun illumination. The results showed that the Target device maintained a highly stable output for 300s. In contrast, the Control devices degraded performance faster than Target devices under light illumination at MPPT. Figure 7b illustrates the self-storage stability of unencapsulated devices storage under dark conditions within the N_2 -filled glove-box at ambient temperature. The Target device maintained 90% of their initial efficiency after 1800 h. In contrast, the Control device retained 45% of its initial efficiency after 1000 h. The Control devices exhibited accelerated degradation at MPPT and during storage.

For TLP solar cells, the uncoordinated Sn^{2+} ions are intrinsically prone to oxidation, which accelerates defect formation and device degradation. The introduction of EDDA effectively suppresses interfacial defects through chelating coordination with under-coordinated Sn^{2+}/Pb^{2+} ions, thereby stabilizing the perovskite lattice throughout the perovskite layer. Those combined effects make Target devices more stable compared to Control devices. Direct evidence of strong coordination between EDDA and tin halides is provided by XRD analysis of SnI_2 -EDDA complexes. As shown in Figure 7c, the characteristic diffraction peak of SnI_2 become weaker after interacting with EDDA and there is a clear shift in peak position. This structural modification confirms that EDDA make strong coordination with SnI_2 , effectively stabilizing Sn^{2+} against oxidation and thereby enhancing the intrinsic stability of the Target devices. The time-dependent oxidation behavior of SnI_2 precursor solutions further corroborates this stabilization mechanism. As shown in Figure 7d, initially, both SnI_2 and $SnI_2 + EDDA$ solution in DMSO solvent exhibited a similar light-yellow color. Both vials with solution were open and storage in an ambient environment. Upon exposure, the SnI_2 solution underwent a rapid color transformation, turning reddish yellow within approximately 20 min, indicating the oxidation of Sn^{2+} [60]. In contrast, the $SnI_2 + EDDA$ solution exhibited a much slower color change, suggesting that EDDA plays a crucial role in maintaining the chemical integrity of the precursor solution. This finding indicates EDDA form coordination bond with SnI_2 and helps to improve the quality of the final perovskite film. This finding is consistent with the previous finding in Figure 2d, Figures 3–5. The high-quality perovskite films enhance the long-term stability of the resulting perovskite devices. To gain a deeper understanding of the oxidation process, we tracked the time-dependent behavior of the solution using UV-vis absorption spectroscopy, as shown in Figure 7e,f. It is well known that Sn^{2+} ions oxidizes more readily than I^- ions due to its lower standard redox potential (0.15 V for Sn^{2+}/Sn^{4+} vs. 0.53 V for $3I^-/I_3^-$) [61]. Cao et al. confirmed that the oxidation of Sn^{2+} generates the Sn^{4+} in the precursor solution [62]. Due to the oxidation of Sn^{2+} in SnI_2 solution, the absorption edge was shifted to the higher wavelength over expose time of solution [63]. In contrast, the $SnI_2 + EDDA$ solution exhibits a much slower spectral

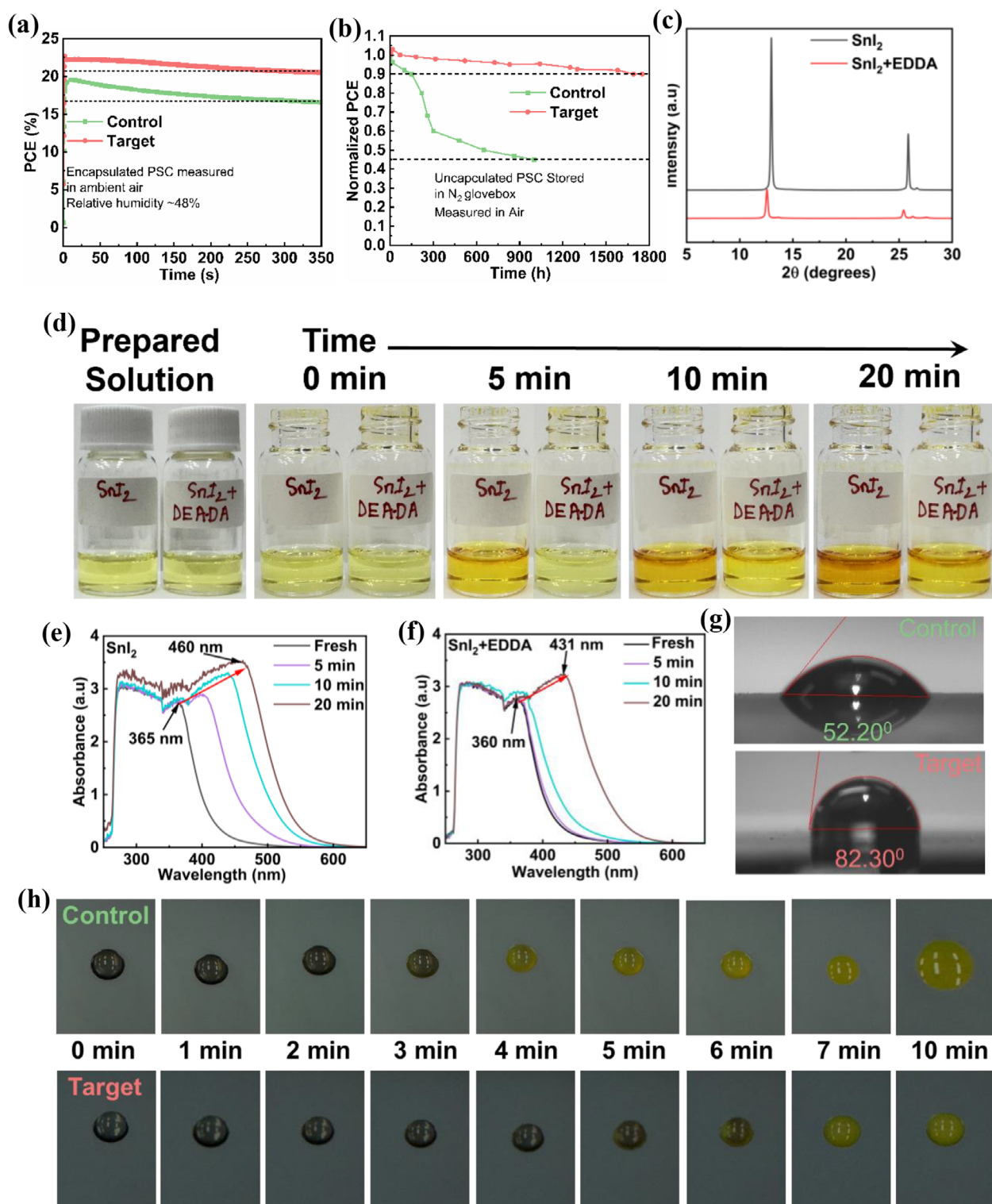


FIGURE 7 | a) Stability of Sn-Pb PSCs at MPPT under one sun condition. b) Storage stability of Sn-Pb PSCs in N₂ environment. c) XRD for SnI₂ and SnI₂ + EDDA thin films. d) Photographic images and e, f) Absorbance of SnI₂ and SnI₂ + EDDA precursor solution in DMSO at different exposed times. g) Water contact angle of TLP films. h) Photographs for time-dependent stability monitoring of TLP films using 5 μL deionized water droplets.

evolution, confirming suppressed oxidation kinetics, in excellent agreement with the visual observations in Figure 7d. Beyond chemical stabilization, EDDA also enhances the environmental robustness of the perovskite films. Water Contact-angle measurements (Figure 7g) show that the Target perovskite film exhibits a larger water contact angle than the Control film, indicating

a more hydrophobic surface. This improvement is primarily attributed to EDDA-induced crystallization modulation at the buried interface, which promotes higher crystallinity, enlarged grain interiors, and a reduced density of grain boundaries. In addition, EDDA post-treatment effectively suppresses surface and interfacial defects, thereby decreasing the density of exposed

polar sites associated with undercoordinated $\text{Sn}^{2+}/\text{Pb}^{2+}$ ions. The combined effects reduce surface polarity and moisture adsorption, leading to improved environmental robustness of the Target perovskite films.

To visualize more deeply the hydration resistance of unencapsulated TLP films, we monitored the real-time degradation when exposed to 5 μL water droplets, as shown in Figure 7h. The Control film exhibited initial signs of decomposition at 3 min and completely transformed into a yellow $\text{PbI}_2/\text{SnI}_2$ -rich phase by 4 min. In contrast, the Target film showed significantly enhanced moisture resistance, maintaining its dark, intact surface throughout the entire 4 min without any noticeable visual degradation. Those findings confirmed that the Target film exhibits significantly enhanced resistance to oxygen and moisture, thereby contributing to the improved operational stability of the Target devices under MPPT and in storage conditions.

3 | Conclusion

In this work, we introduced a synergistic interfacial engineering approach that sequentially addresses the buried interface and top perovskite surface using the multifunctional molecule EDDA. The presence of dual $-\text{NH}_3^+$ and $-\text{COO}^-$ groups reduces the inherent acidity of PEDOT:PSS and facilitates hydrogen bond and forms strong chelating interaction with $\text{Pb}^{2+}/\text{Sn}^{2+}$. This coordination effectively modulates buried interface potential, reduces crystal nucleation concentration, promotes orderly crystal growth and enhanced TLP film quality. The chemical polishing of the perovskite top surface inhibits the Sn^{2+} oxidation, reduces defects and facilitates more efficient charge extraction. The synergistic effects reduce interfacial defects, improves the perovskite quality and suppresses the trap-assisted recombination. Ultimately, the Target TLP solar cells achieved a PCE of 23.30% with improved V_{OC} and FF. This study presents a dual-site coordination strategy as a framework for tailoring interfacial chemistry in mixed TLP, providing insights into molecular bridge-mediated defect passivation and enhancement of stability.

4 | Experimental Section

Experimental details are provided in the Supporting Information.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supporting File: sml173119-sup-0001-SuppMat.pdf.