Inorganic perovskite/organic tandem solar cells with 25.1% certified efficiency via bottom contact modulation

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Abstract

Wide bandgap perovskites in monolithic perovskite/organic tandem solar cells face challenges like unregulated crystallization, severe defect traps, poor energetic alignment, and undesirable phase transitions, primarily due to unfavorable bottom interfacial contact. These issues lead to energy loss and device degradation. In this study, we synthesize acidic magnesium-doped tin oxide quantum dots to modulate the bottom interface contact in wide bandgap $CsPbI_2Br$ perovskite solar cells. This design balances physical, chemical, structural, and energetic properties, passivating defects, optimizing energy band alignment, enhancing perovskite film growth, and mitigating instability. We also elucidate the instability mechanism caused by alkaline-based tin oxide bottom contact, emphasizing the impact of tin oxide solution's acid/base properties on the stability and performance of the device. Consequently, the wide bandgap $CsPbI_2Br$ solar cell achieve a power conversion efficiency of 19.2% with a 1.44 V open-circuit voltage. The perovskite/organic tandem solar cell demonstrates an efficiency of 25.9% (certified at 25.1%), with improved stability under various conditions.

Introduction

Tandem solar cells (TSCs) hold immense potential for more efficient solar spectrum utilization, minimizing thermalization loss, and surpassing the theoretical single-junction cell efficiency limit, potentially achieving a power conversion efficiency (PCE) greater than 40%[1]. Recently, monolithic perovskite-based TSCs have attracted tremendous interest in the photovoltaic (PV) field[2-7]. Advances in materials design, perovskite precursor engineering, and fabrication techniques have led to notable progress in perovskite-based TSCs. However, challenges such as energy-intensive processes, lack of flexibility, and rapid Sn^{2+}/Sn^{4+} oxidation hinder their commercial potential. On the other hand, perovskite/organic TSCs (POTSCs) offer advantages like cost-effectiveness, easier manufacturing, use of orthogonal solvents, improved stability of sub-cells, low-temperature processing, and better flexibility[8-13]. Despite these benefits, POTSCs lag behind current perovskite/c-Si (33.9%)[14] and all-perovskite (29.4%)[15] TSCs in development.

Currently, bromine-rich mixed cation-based POTSCs with a p-i-n architecture lead the field, boasting a promising PCE of 25.22% (certified at 24.27%)[16] and an impressive PCE of 25.82% (certified at 25.06%)[17]. Given that state-of-the-art organic solar cells (OSC) have a bandgap of approximately 1.33 eV[12], the theoretically ideal pairing would be wide-bandgap (WBG) perovskites with a bandgap around 1.9 eV, a criterion perfectly met by all-inorganic $CsPbI_2Br$. These perovskites offer excellent thermal stability, simple composition, antisolvent-free processing, and reduced phase segregation compared to bromine-rich hybrid WBG perovskites[18-21]. However, challenges remain with $CsPbI_2Br$ perovskite solar cells (PSCs), such as unsuitable phase transitions, unwanted crystallization, buried pinholes, high defect density, and poor energy alignment, leading to significant voltage loss and limiting efficiency to 24%[11]. The voltage losses in WBG $CsPbI_2Br$ perovskites are linked to phase instability, defect traps, and poor bottom contact interfaces. These issues cause poor energy alignment and severe interfacial recombination, resulting in low-quality crystal growth[22-25]. The bottom interfacial contacts, acting as defect reservoirs, threaten the long-term stability of PSCs[22,26]. Addressing poor energy alignment and interfacial trap states is crucial for minimizing voltage deficits, maximizing performance, and ensuring stability in both single-junction PSCs and POTSCs. Common bottom electron transport layer (ETL) contacts for medium bandgap (<1.6 eV) are ineffective in WBG $CsPbI_2Br$ PSCs due to shifted conduction band minimum (CBM) and unique defect properties, leading to poor energy alignment and inefficient defect passivation.

In this work, we merge experimental and theoretical methods to achieve the rational design of bottom contact modulation and elucidate the underlying mechanism of interface-induced instability issues. We developed an acidic magnesium-doped tin oxide quantum dots (M-SQDs) ink for effective bottom contact modulation in WBG $CsPbI_2Br$ PSCs. This engineered interface improves energy band alignment, passivates defects, enhances perovskite film growth, and reduces instability. Utilizing this approach, we achieved a high PCE of 19.17% for $CsPbI_2Br$ PSCs, with only a 0.43 V photovoltage loss. We also achieved high performance POTSCs with an impressive PCE of 25.90% (certified at 25.08%) and a V_{OC} of 2.21 volts. The tandem device showed excellent stability, maintaining 85% of its performance for 1000 hours under 1-sun illumination at 45°C ± 5°C and 70% humidity. Additionally, the POTSCs retained 95% PCE after 200 thermal cycles between -40°C and 85°C.

Properties of M-SQDs with adjustable features

Magnesium acetate tetrahydrate was chosen as a dopant for SQDs ink due to its adaptable properties. We explored its potential for modulating bottom ETL contacts in WBG $CsPbI_2Br$ PSCs, focusing on its impact on photovoltage loss and stability. **Figure 1a** shows the morphology of M-SQDs via transmission electron microscopy (TEM). These M-SQDs, averaging 2-5 nm in size, display clear lattice fringes, indicating high quality, which is beneficial for creating a continuous, defect-free ETL on the textured FTO surface[22]. The selected area electron diffraction (SAED) pattern in **Fig. 1a** corresponds to the (110), (101), (211), and (310) crystal planes of SnO_2, suggesting superior crystallinity, as further confirmed by X-ray diffraction (XRD) results in **Fig. 1b**. The peaks align with a tetragonal structure, confirming pure SnO_2 crystal formation.

Energy-dispersive X-ray spectroscopy (EDS) in **Fig. 1a** shows uniform Mg distribution within the SQDs. The crystal structure remains unchanged and free of impurities[27]. Notably, M-SQDs have a higher chlorine anion (Cl^-) concentration than undoped counterparts (**Supplementary Fig. 1-2**), which helps reduce trap state density at the ETL-perovskite interface[28]. The C=O bond's stretching vibration disappears after $MgAc_2·4H_2O$ doping, and Cl^- concentration increases with more doping, indicating a Cl^- fixation effect (**Supplementary Fig. 3**) due to the high acid dissociation constant (pKa) of acetic acid in an acidic environment[29] (**Supplementary Table 1**). X-ray photoelectron spectroscopy (XPS) reveals divalent Mg^{2+} in SQDs (**Supplementary Fig. 3**), with Mg^{2+} electron donation shifting the Sn 3d signal to lower binding energy, reducing the cationic charge of under-coordinated Sn^{2+} in SnO_2 (**Supplementary Fig. 4**). **Figure 1c** shows the O 1s spectrum deconvoluted into three peaks[30]: lattice oxygen (O_L) in SnO_2, oxygen vacancies (O_V), and hydroxyl groups (O_H) on the SnO_2 surface. Oxygen vacancies and hydroxyl groups can enhance electron capture and create barriers for electron transport[31]. Notably, the proportion of -OH species decreases from 11.68% to 8.99% after Mg^{2+} doping, improving bottom contact.

We examined the energy level of the M-SQDs layer using ultraviolet photoelectron spectroscopy (UPS) (**Supplementary Fig. 5-6**). Mg^{2+} doping raises the energy levels of SnO_2 (**Fig. 1d**). Notably, a conduction band offset plus (CBO+) structure forms when the conduction band minimum (CBM) of SnO_2 with 0.01 M Mg^{2+} (0.01M-SQD) exceeds that of $CsPbI_2Br$ (**Fig. 1d**)[32]. Compared to undoped SQDs, the work function of 0.01M-SQDs is higher than that of $CsPbI_2Br$, creating a 0.09 eV offset. Kelvin probe force microscopy (KPFM) confirms this, showing an increased contact potential difference (CPD) for 0.01M-SQDs, indicating a slight upward shift in work function after Mg^{2+} doping (**Supplementary Fig. 7**). We propose a band alignment schematic to elucidate the critical role of the CBO+ structure in the WBG perovskite system (**Fig. 1e**). The CBO- structure, formed by aligning the energy levels of undoped SQDs and perovskite, acts as a barrier to carrier transport, leading to carrier accumulation at the ETL/perovskite interface. This accumulation can increase recombination through interfacial defects, causing a significant open-circuit voltage (V_{OC}) deficit. In contrast, the CBO+ structure enhances band bending in the ETL's CB, reducing charge carrier recombination at the interface and minimizing photovoltage loss.

It is universally accepted that the formation of tin interstitial (Sn_i) and oxygen vacancy (V_O) defects, which create an n-type semiconductor, significantly influence the conductivity and energy level of undoped SnO_2[31,33]. To understand how Mg doping influences SnO_2 properties, we used density functional theory (DFT) simulations to study the formation energies of Sn_i and V_O under different doping conditions (**Fig. 1f**). Substitutional Mg doping, where Sn^{4+} is replaced by Mg^{2+}, is likely due to their similar ionic sizes, while interstitial Mg defects are more common at high dopant levels[34]. As shown in **Fig. 1g**, the formation energies of Sn_i and V_O decrease significantly, from 6.31 eV to 1.54 eV and 3.75 eV to 1.01 eV, respectively. The reduction in the defect formation energies (DTEs) suggests that Sn_i and V_O defects are easily produced by Mg substitutional doping, enhancing the electrical conductivity of the SnO_2 film. However, at high Mg concentrations, interstitial Mg defects can form, increasing Sn_i and V_O formation energies and compromising the material's properties[31]. Importantly, DFT simulations suggest that hydroxyl groups on the SnO_2 ETL surface lower the DFE of V_O and Sn_i (**Supplementary Fig. 8**). Mg doping reduces these hydroxyl groups, helping to prevent surface defects and suppress interfacial non-radiative recombination.

$CsPbI_2Br$ perovskites on modulated bottom contacts

We profiled the distribution of Mg^{2+} across the interface between perovskite and SQDs using time-of-flight secondary-ion mass spectrometry (ToF-SIMS). As demonstrated in **Fig. 2a**, we detected Mg^{2+} at a certain thickness before Sn^{2+}, indicating that Mg^{2+} can diffuse from the SnO_2 film into the perovskite during annealing. This diffusion was also confirmed by FIB-TEM-EDS and glow discharge-optical emission spectroscopy (GD-OES) (**Supplementary Fig. 9-10**). Moreover, we conducted the angle-dependent GIWAXS measurements on perovskite films deposited on both SQD substrate and M-SQD substrate (**Supplementary Fig. 11**). The introduction of Mg helps achieve a uniform lattice constant and suppresses lattice mismatch throughout the entire thickness of the perovskite film. This Mg^{2+} diffusion is beneficial for low-dose B-site doping and effectively minimizes defect states in $CsPbI_2Br$ perovskites[35]. In contrast, no Mg^{2+} signal was detected in the control sample (**Supplementary Fig. 12-13**).

We also used in situ UV-vis spectrometry to study the effect of Mg^{2+} on the crystallization of $CsPbI_2Br$ film during annealing at 120 °C (**Fig. 2b**). Absorption at wavelengths exceeding 420 nm increased rapidly with annealing time, indicating a phase transition from the wet precursor film to the α-phase. We extrapolated the absorption intensity at the 500 nm to amplify the disparity between the perovskite films deposited on SQDs and M-SQDs films (**Fig. 2c**). Notably, the perovskite film on M-SQDs initiated crystallizing at 18 seconds, later than the film on pristine SQDs, which started at 11 seconds. This delay indicates that M-SQDs slow down crystallization, leading to higher-quality inorganic perovskite films with fewer defects. Numerous research studies echo a similar trend, suggesting that divalent Lewis acid metal ions can slow crystallization, enhance grain size, improve crystal quality, mitigate both shallow and deep-level defect states, and prolong the stability of all-inorganic perovskites via subtle B-site doping[36,37].

To understand the effect of the divalent Mg^{2+} modulated interface on the morphology and quality of the perovskite film, we conducted optoelectronic and structural characterizations of $CsPbI_2Br$ films on modified bottom contacts. Scanning electron microscopy (SEM) images reveal that the Mg-doped substrate significantly influences the perovskite morphology, resulting in a smoother surface with enlarged perovskite domains on the optimized M-SQDs (**Fig. 2d** and **Supplementary Fig. 14**). The perovskite film on M-SQDs completely envelops the substrate, unlike the film on pristine SQDs, which has many pinholes likely due to the poor wettability (**Supplementary Fig. 15-16**). We then utilized confocal steady-state photoluminescence (PL) mapping measurements to assess the quality of the perovskite films (**Fig. 2e**). We observed a more uniform and brighter PL intensity distribution in the perovskite film with M-SQDs contacts compared to the control, suggesting fewer defects in the optimal M-SQDs-based perovskite film.

The improved film quality and the crystal structure were further verified by X-ray diffraction (XRD), as shown in **Supplementary Fig. 17**. It is noted that the peak positions appearing at 14.65° and 29.56° correspond to the (100) and (200) planes of α-$CsPbI_2Br$, respectively[38]. To further assess orientation and crystallinity, we conducted grazing incidence wide-angle X-ray scattering (GIWAXS) measurements and determined the corresponding intensity profiles in the q_z direction for the (100) plane and the polar angle (χ) along the (110) ring (**Fig. 2f-h**). The increase in scattering intensity and the reduction in polar angle peak width indicates that the crystallinity and orientational order can be significantly improved by utilizing optimized M-SQDs bottom contacts.

Charge carrier dynamics at the bottom interface

To better understand the superior performance of the bottom contact modulation, the charge carrier dynamics between ETL and the perovskite film were investigated. We first used steady-state photoluminescence (PL) and time-resolved PL (TRPL) spectra to examine the $CsPbI_2Br$ film on the modulated contact. The results showed significantly quenched PL and a reduced lifetime (**Supplementary Fig. 18 and Supplementary Table 2**), demonstrating the superior electron-extraction ability of the M-SQDs contact ETLs[39]. Next, we then used ultrafast transient absorption spectroscopy (TAS) to further explore carrier transport dynamics (**Supplementary Fig. 19**). We photoexcited $CsPbI_2Br$ films on different modulated bottom contacts at 400 nm over the wavelength range of 450-800 nm. The M-SQDs-based perovskite film displayed a faster decrease in bleaching peak intensity compared to the control, indicating a shorter exciton lifespan due to more efficient carrier transport. This enhanced charge extraction was also confirmed by transient time-resolved microwave conductivity measurement (TRMC), a non-destructive method to probe the charge-carrier dynamics in semiconductor films[40]. We found that $CsPbI_2Br$ films on M-SQDs bottom contacts showed shorter carrier lifetime and reduced carrier mobility compared to the control sample (**Supplementary Fig. 20**), indicating enhanced charge transportation.

We use benchmark commercial SnO_2 (Com-SnO_2) ETLs, extensively utilized in planar PSCs[41], as a comparison. It was found that our synthesized SQDs-based contact ETL exhibited higher electron mobility compared to Com-SnO_2 (**Supplementary Fig. 21**).

Consequently, the perovskite film with SQDs demonstrated a greater charge extraction capacity than the film based on Com-SnO_2, as evidenced by the quenched PL intensity and shorter lifetime (**Supplementary Fig. 22 and Supplementary Table 3**). Additionally, we performed XRD to assess the quality of films deposited on the substrates with Com-SnO_2, SQDs and M-SQDs contact ETL. The M-SQDs-based $CsPbI_2Br$ perovskite film exhibited a higher peak intensity of the (100) and (200) planes compared with the Com-SnO_2 one, suggesting that M-SQDs-based bottom contact ETL contributes to improving the crystal quality perovskite films (**Supplementary Fig. 23**). This is also supported by a lower trap density in M-SQDs-based $CsPbI_2Br$ perovskite (**Supplementary Fig. 24**), as revealed by thermal admittance spectroscopy measurements.

Film degradation mechanism on alkaline/acidic substrates

Besides achieving high performance of the perovskites, stability is equally critical for their commercial application. We found that the acid-base property of the SnO_2 solution significantly influences perovskite stability. The M-SQDs-based solution is acidic with a pH of ~0.8, while the Com-SnO_2 solution is alkaline with a pH of 11.35 (**Supplementary Fig. 25**). We deposited WBG $CsPbI_2Br$ films on different SnO_2 bottom contact ETLs and aged them under high humidity (approximately 60% RH) for various durations (**Supplementary Fig. 26**). The $CsPbI_2Br$ films deposited on SQDs demonstrate superior humidity stability compared to those on Com-SnO_2. The M-SQDs-based perovskite film shows no obvious degradation over 360 minutes, while the Com-SnO_2-based film degraded in just 5 minutes. This indicates that the perovskite film with M-SQDs bottom contact offers excellent humidity stability, which can be attributed to improved film quality and strengthened bottom interface contact.

We suspect that the poor humidity stability of Com-SnO_2-based perovskite film is directly related to its alkalinity of bottom contact. To validate our hypothesis, we conducted stability tests on various perovskite films. These included H_2O-doped perovskite film on FTO, HI-doped perovskite film on FTO, KOH-doped perovskite film on FTO, and perovskite film on KOH-coated FTO. Our findings revealed that the perovskite film in direct contact with a KOH-treated surface demonstrated the least stability in a humid environment (**Supplementary Fig. 27**). The stability of the alkali-doped perovskite precursor was also found to be inferior compared to the control and acid-doped samples. This suggests that the instability of perovskites may be linked to alkalinity. It is important to note that the impact of K^+ on perovskite stability was excluded from the test (**Supplementary Fig. 28**), as the perovskite film deposited on the KCl-coated FTO displayed good humidity stability.

The main challenge for inorganic PSCs is maintaining phase stability issue under humidity. To further elucidate the degradation pathway of the $CsPbI_2Br$ perovskite, we employed depth-dependent GIWAXS measurements to track the photovoltaic α and non-photovoltaic δ phases from the top to the bottom of the films. Fresh perovskite films, which are atop bottom contacts (Com-SnO_2 and M-SQDs), were subjected to accelerated aging at a relative humidity (RH) of 70% (**Supplementary Fig. 29**). This process led to the induction of moderate degradation. As depicted in **Fig. 3**, an incident angle of 0.2° (0.4° or 1°) allows for detecting approximately 80 nm (200 nm or 600 nm) film thickness[42]. We observed the diffraction ring of the δ-phase at $q_z = 0.72$ Å^{-1} in Com-SnO_2-based perovskite films. Clearly, the intensity of the δ-phase diffraction ring amplified as the incident angle increased, indicating that the bottom interface is prone to δ-phase formation. In contrast, for the M-SQDs-based perovskite film, no evident indication of the δ-phase was detected in either the degraded or fresh film.

It is widely accepted that the phase content is directly proportional to the intensity of the XRD peak. Therefore, we selected the diffraction rings of the δ-phase ($q_z = 0.72$ Å^{-1}), the (100) plane of the α-phase ($q_z =1.05$ Å^{-1}), and the (110) plane of the α-phase ($q_z =1.50$ Å^{-1}) to integrate the intensity and quantitatively profile the distribution of the δ-phase throughout the degraded film (**Supplementary Fig. 30 and 31**). Consequently, the integrated intensity of Δδ and Δα was methodically calculated to ascertain the proportion of the δ-phase within different depth region ranges (**Supplementary Table 4**). We interestingly found that the percentage of the δ-phase near the bottom contact interface was higher than that in the middle and top surface film, irrespective of the film's condition, whether fresh or degraded. This confirms that the bottom contact interface films are more susceptible to degradation. Notably, the δ-phase content near the bottom contact interface of Com-SnO_2-based perovskite film was significantly higher than that of the M-SQDs-based perovskite film, indicative of an alkaline substrate that readily induces the non-photovoltaic phase and triggers the degradation. The δ-phase content increased dramatically at the bottom of the film, likely due to imperfect bottom contact facilitating δ-phase formation.

To better understand the degradation mechanism at the bottom interface, we investigated the acidity and alkalinity of secondary dissolution in various SnO_2-precipitated powders (**Supplementary Fig. 32**). We conducted qualitative acid-base analyses on these re-dispersed SnO_2 solutions using phenolphthalein reagent, litmus reagent, and pH test paper. The experimental results indicate that the re-dispersed SnO_2 retain their respective acidity and alkalinity in the solution; these properties are likely linked to the surface ligands of SnO_2 (**Supplementary Fig. 33**). We analyzed how an alkaline environment affects perovskite stability, focusing on both perovskite precursors and the resulting films. It was found that only the perovskite precursor with KOH produced precipitation, unlike the others, indicating a strong interaction between alkaline-based solutions and the perovskite precursor (**Supplementary Fig. 34**). Furthermore, we examined the interaction between the alkaline KOH medium and the separate components of the perovskite precursor (e.g., PbI_2, $PbBr_2$, and CsI). Noticeably, it was observed that both PbI_2 and $PbBr_2$ solutions with KOH generated precipitation identified as lead-oxygen compounds.

To avoid the impact of humidity, the experiment was conducted in a nitrogen-filled glovebox (**Supplementary Fig. 35**). We observed that $CsPbI_2Br$ perovskite films treated with a KOH-ethanol solution exhibited rapid degradation, evidenced by a colour change from brown to yellowish, indicating that an alkaline-based solution decomposes the perovskite film and damages its structure. Noticeably, XRD patterns of the degraded perovskite films with alkaline KOH post-treatment showed the disappearance of the main peak of $CsPbI_2Br$ perovskite and the emergence of an additional CsI characteristic peak. Similarly, we examined the interaction between alkaline KOH and the separate components-based films. Significant colour changes were noted in lead halides (e.g.,

$PbBr_2$ and PbI_2) after KOH solution treatment, revealing that alkaline KOH decomposes lead halides. In addition, The H^+-rich substrates are highly effective in preventing OH^- induced degradation and significantly improving the stability of perovskite film (**Supplementary Fig. 36**). Therefore, perovskites on alkaline-based ETL substrates tend to suffer more severe degradation than those on acidic-based ETL substrates.

The mechanism of degradation of perovskite films prepared with alkaline and acidic substrates in a highly humid environment is illustrated in **Figure 3g** and **h**. It is well known that in high-humidity environments, the grain boundaries and pinholes at the buried interface of perovskite/substrates become primary pathways for water molecules to penetrate[43,44]. For the alkaline substrate (Com-SnO_2), the OH^- ions accelerate dissociation from the alkaline substrate when the moisture reaches the substrate. These dissociated OH^- ions rapidly interact with Pb^{2+} ions in the perovskite lattice, destroying the perovskite lattice and creating numerous defects at the buried interface. This process results in an accelerated phase transition from the cubic phase to the delta phase at the bottom of the perovskite film[45,46]. In contrast, the acidic substrate (SnO_2 QDs) prevents the formation of OH^- ions at the buried interface, inhibiting the phase transition when the perovskite film is exposed to moisture. As a result, perovskite films prepared with the acidic substrate (SnO_2 QDs) exhibit excellent humidity stability compared to those prepared on the alkaline substrate.

More importantly, this interesting phenomenon is not limited to inorganic perovskites. We also observed a similar phenomenon in the high-performing narrower bandgap (1.53 eV) hybrid perovskite system. As shown in **Supplementary Fig. 37**, KOH (alkaline)-treated bottom contact substrates can trigger the formation of the yellow δ-phase, consequently escalating the $FA_{0.85}MA_{0.15}PbI_3$ film's instability and impacting its performance. Notedly, bottom contacts (Com-SnO_2, SQDs, and M-SQDs) were implemented to fabricate $Cs_{0.03}(FA_{0.97}MA_{0.03})_{0.97}Pb(I_{0.97}Br_{0.03})_3$-based solar cells (1.53 eV). All detailed photovoltaic parameters are summarized in **Supplementary Fig. 38 and Supplementary Table 5**. The devices based on M-SQDs achieved an impressive PCE of 25.01%, coupled with a high fill factor (FF) of 82.91%, V_{OC} of 1.18 V and J_{SC}

of 25.46 mA/cm^2. As a comparison, devices based on Com-SnO_2 and SQDs exhibited a larger photovoltage loss, leading to inferior photovoltaic performance.

Single junction $CsPbI_2Br$ PSCs and OSCs

We optimized the device's performance by fine-tuning the doping concentration of the bottom contact ETL (**Supplementary Fig. 39 and Supplementary Table 6**). We constructed WBG $CsPbI_2Br$ devices using Com-SnO_2, SQDs, and M-SQDs as the bottom contact ETL, with the dopant-free polymer PTQ10 as the hole transport layer (HTL) (**Supplementary Fig. 40**). The corresponding current density-voltage (J-V) curves and PV parameters are detailed in **Fig. 4a** and **Supplementary Table 7**. The V_{OC} for the champion device (M-SQDs) reached an impressive 1.44 V, signifying an impressively low V_{OC} loss for the 1.88 eV perovskite, while the undoped (SQDs) and Com-SnO_2-based devices yielded a V_{OC} of 1.37 V and 1.34 V, respectively. We attribute this enhanced V_{OC} to the adoption of the CBO+ structure and the suppression of defect state formation by Mg doping of the bottom contact. Consequently, the M-SQDs contact ETL-based $CsPbI_2Br$ PSC achieved a high PCE of 19.17%, outperforming both the SQDs and the Com-SnO_2-based devices (**Fig. 4b and Supplementary Fig. 41**). The integrated photocurrent density, calculated from the external quantum efficiency (EQE) spectra, aligns well with the short-circuit current density (J_{SC}) value from the J-V curves (**Fig. 4c and 4d**).

We employed electroluminescence EQE (EQE_{EL}) to evaluate the non-radiative recombination loss of the device (**Fig. 4e**) under the light-emitting diode (LED) working mode. The M-SQDs-based device exhibited a higher EQE_{EL} than the other two types of devices, indicating a reduced non-radiative recombination loss[47]. The optical bandgap (1.88 eV) of WBG $CsPbI_2Br$ perovskite was determined by the maximum point of the EQE spectra derivative (**Supplementary Fig. 42**)[48,49]. Remarkably, the M-SQDs-based device delivers a maximum V_{OC} of 1.45 V, i.e., an impressively low photovoltage loss of 0.43 V, with V_{OC} exceeding 90% of the detailed balance (DB)-limit compared to the reported values (**Fig. 4f, Supplementary Fig. 43, and Supplementary Table 8**). For constructing POTSCs, we selected the state-of-the-art

PM6: BTP-eC9 system as the light absorber for the bottom sub-cell (**Fig. 4g**). To maximize the performance of the OSCs, a crystallization regulating additive (e.g., TCB) was incorporated into the PM6: BTP-eC9 system[50]. The optimized device achieved an impressive PCE of 18.90% with an n-i-p architecture (**Fig. 4h**), and the corresponding EQE and integrated J_{SC} are displayed in **Fig. 4i**.

Monolithic n-i-p all-inorganic POTSCs

Building on the success of reduced photovoltage loss in $CsPbI_2Br$ (1.88 eV) PSCs with M-SQDs contact ETLs, we further developed monolithic POTSCs. These tandem cells featured a device structure comprising a glass substrate/m-FTO/M-SQDs/$CsPbI_2Br$/PTQ10/MoO_X/Ag/ZnO/PFN-Br/PM6: BTP-eC9/MoO_X /Ag (**Fig. 5a**). The transfer matrix formalism (TMF) simulation results (**Supplementary Fig. 44**) show that that optimal sub-cell thicknesses can achieve high J_{SC} in POTSCs. Performance comparisons of POTSCs with Com-SnO_2, SQDs, and M-SQDs are in **Supplementary Fig. 45**, with corresponding PV parameters in **Supplementary Table 9**. **Fig. 5b** shows the current density-voltage (J-V) curves of the best-performing POTSCs with M-SQDs-based contact ETL (**Supplementary Table 10**). The champion M-SQDs-based tandem solar cell achieved an encouraging PCE of 25.90%, with an impressively high V_{OC} of 2.21 V, J_{SC} of 14.51 mA cm^{-2}, and FF of 80.77%. The device efficiency was further certified at the Shanghai Institute of Microsystem and Information Technology (SIMIT) with a PCE of 25.08% (**Supplementary Fig. 46**). The steady-state power output (SPO) showed the devices with stabilized PCEs of 25.61% (**Supplementary Fig. 47**). Notably, the bottom contact modulation strategy resulted in the highest V_{OC} of 2.27 V for POTSCs (**Supplementary Fig. 48 and Supplementary Table 11**), which is a benchmark value to the best of our knowledge. We fabricated M-SQDs-based tandem devices, yielding an average PCE of 24.90%, which surpasses the average PCE of undoped devices (22.11%) and Com-SnO_2-based devices (17.86%) (**Supplementary Fig. 49**). **Figure 5c** depicts the EQE spectra of the M-SQDs-based tandem device, delivering an integrated J_{SC} of 14.23 mA cm^{-2} for the WBG top cell and 14.04 mA cm^{-2} for the NBG bottom cell, respectively.

We further evaluated the operational stability of encapsulated POTSCs under light illumination. The MPP output was continuously monitored under one-sun irradiation using a light-emitting diode (LED) array (**Fig. 5d**). The M-SQDs-based tandem devices retained 85% of their initial performance after 1000 hours of MPP tracking at 45±5 °C and ~70% RH. In contrast, undoped-SQDs-based tandem devices maintained 80% PCE after 145 hours, and the Com-SnO_2-based tandem devices showed a rapid PCE decline with the first 24 hours. We used PL spectra to investigate the phase segregation in WBG perovskite films prepared with Com-SnO_2 and M-SQDs under light exposure (**Supplementary Fig. 50-52**). The M-SQDs based inorganic perovskite film exhibits the most outstanding tolerance for halide phase segregation.

In thermal cycling tests between −40°C and 85°C, Com-SnO_2-based samples decayed to 70% of their initial efficiency after 200 cycles, while SQD-based samples demonstrated relatively good stability. Especially, the M-SQD-based samples maintained over 95% of their efficiency after 200 cycles (**Fig. 5e**). Despite significant advancements in the stability of acidic M-SQDs-based perovskite/organic tandem devices, various factors persistently contribute to their degradation. This degradation is predominantly associated with the top cell, the interconnection layer, and the bottom cell, where defect-induced deterioration is particularly pronounced. On the other hand, considering OSC bottom cell photo degradation is significantly reduced thanks to the UV-blocking nature of perovskite top cell[10], and the superior thermal stability of non-fullerene OSC, the degradation of tandem solar cells is more likely affected by the degradation of perovskite top cell.

In summary, bottom interfacial contacts are crucial for the performance and stability of perovskite devices. We successfully modulated the bottom interface using effective acidic M-SQDs in inorganic WBG $CsPbI_2Br$ PSCs, achieving a high PCE of 19.17% and a low photovoltage loss of 0.43 V. This approach is also effective in other perovskite systems. We identified that the acid-base properties of the SnO_2 solution significantly affect perovskite stability. Additionally, we demonstrated POTSCs with modulated bottom contacts in $CsPbI_2Br$ PSCs, achieving an impressive PCE of 25.90%

(certified at 25.08%), a remarkably high V_{OC} of 2.27 V, and excellent thermal and operational stability.

Methods

Materials

Dimethylformamide (DMF), dimethyl sulfoxide (DMSO), Calcium chloride ($CaCl_2$), 2-(2-aminoethyl) isothiourea dihydrobromide (2AT), Magnesium acetate tetrahydrate ($MgAc_2$:$4H_2O$), Zinc oxide nanoparticles were purchased from Sigma Aldrich. Tin (IV) oxide (15% in H_2O colloidal dispersion), and tin (II) chloride dihydrate were purchased from Alfa Aesar. Titanium chloride ($TiCl_4$) was purchased from Aladdin. Lead acetate ($PbAc_2$) was purchased from Xi'an Polymer Light Technology in China. Cesium iodide (CsI), lead bromide ($PbBr_2$), and lead iodide (PbI_2) were purchased from Advanced Election Technology Company in China. PM6, BTP-eC9, PTQ10, and PFN-Br were purchased from Solarmer Energy Inc. 1,3,5-trichlorobenzene (TCB) was purchased from Tokyo Chemical Industry Co., Ltd. All the chemicals are used directly without further purification.

Synthesis of $PbX_2(DMSO)_x$

The $PbI_2(DMSO)_2$ and $PbBr_2$ (DMSO) were prepared in the lab, following the method outlined in a previous report[78]. Initially, 5 g of PbI_2 (or $PbBr_2$) was dissolved in 15 mL DMSO, with the solution being heated and stirred at 60°C. Subsequently, 50 mL of toluene was added to the PbI_2 or $PbBr_2$ solution, resulting in the formation of a white precipitate. This precipitate was then filtered and dried in a vacuum oven at 60°C for a period of 24 hours.

Synthesis of Mg-doped SnO_2 QDs

The SnO_2 QDs were prepared in the lab following our previous recipe[22]. Specifically, a SnO_2 QDs precursor (0.13 M) was prepared by dissolving 2-(2-aminoethyl) isothiourea hydrobromide and $SnCl_2$:$2H_2O$ in deionized water, maintaining a fixed molar ratio of 1:6.5. This was followed by a minimum of 2 hours of vigorous stirring in an oxygen-rich environment at room temperature. Mg-doped SnO_2 QDs with different doping concentrations (0.005 M, 0.01 M, 0.02 M) were synthesized by adding $MgAc_2$:$4H_2O$ during the preparation of the SnO_2 QDs precursor, following the same procedure.

Fabrication of WBG all-inorganic PSCs and POTSCs

The m-FTO substrate was prepared via a chemical approach[79]. Firstly, the FTO substrates were sequentially cleaned with isopropanol, acetone, and ethanol in an ultrasonic bath for 30 minutes. The substrates were then immersed in a $TiCl_4$ diluent solution (4.5 mL $TiCl_4$ in 200 mL deionized water) and annealed at 70°C for 30 minutes. The SnO_2 QDs, doped with varying concentrations of Mg^{2+}, or Com-SnO_2 (achieved by adding SnO_2 colloidal dispersion into deionized water at a volume ratio of 1:5), were spin-coated onto the m-FTO at 4000 rpm for 30 seconds. This was followed by heating at 200°C for 60 minutes to form the ETL layer. The $CsPbI_2Br$ perovskite precursor (1M) was prepared by dissolving $PbBr_2$(DMSO), PbI_2(DMSO), CsI, $PbAc_2$, and $CaCl_2$ (molar ratio = 1:1:2:0.015:0.005) in a mixed solvent of DMF and DMSO (17:3, v/v)[37]. After spin-coating the $CsPbI_2Br$ perovskite precursor onto the substrate at 1000 rpm for 10 seconds and 4000 rpm for 40 seconds, the wet precursor film was sequentially annealed at 35°C for 6 minutes, 120°C for 10 minutes, and 180°C for 3 minutes. Subsequently, PTQ10 (10 mg/mL in chlorobenzene) mixed with carbon nanotubes (0.05 mg/mL) was applied on top of the $CsPbI_2Br$ perovskite layer to form the HTL. Finally, the top electrode was prepared by evaporating 80 nm of Au onto the film. The active area of each device was 0.03 cm^2. For the tandem device, a 6 nm layer of MoO_x was thermally evaporated onto the WBG perovskite subcell after the deposition of PTQ10. This was followed by the deposition of a 1 nm layer of Ag on top of the film, serving as a recombination layer, achieved through thermal evaporation. Subsequently, ZnO nanoparticles and PFN-Br were deposited onto the film. The organic precursor solution, prepared by mixing 8.2 mg of PM6, 9.8 mg of BTP-eC9, and 10 mg of TCB in 1 mL of chloroform, was then dynamically spin-coated onto the substrate at 2500 rpm. The device was then thermally annealed at 100°C for 5 minutes. Finally, the semi-finished cell was transferred into a thermal evaporation chamber with a base pressure of less than 2×10^{-4} Pa, where a 2 nm layer of MoO_x and a 100 nm layer of Ag were deposited through a shadow mask, resulting in an active area of approximately 0.09 cm^2.

Solar cell characterization:

JV measurement

The J-V characteristics of the devices were measured using a Keithley 2400 source meter unit under a calibrated solar simulator from Enli Technology Co. Ltd, equipped with an AM 1.5 filter. It should be noted that the J-V curves were obtained within the range of 1.6 to -0.1 V for the WBG single junction, -0.1 to 1.2 V for the NBG single junction, and 2.3 to -0.1 V for the tandem device, for both reverse and forward scans. Anti-reflection MgF_2 films were utilized during the measurement.

EQE measurement

The measurements were conducted using a QE-R3011 system from Enli Technology Co. Ltd. The single junction devices were measured under monochromatic light, split from 300 nm to 900 nm with a step size of 10 nm. As for the EQE of the tandem cells, the WBG perovskite front cells were measured using an 800 nm polarized optical filter, while the organic bottom cells were saturated with continuous light from a halogen lamp. The WBG organic bottom cells were measured while the perovskite front cells were saturated with constant light from a halogen lamp, using a 550 nm polarized optical filter.

EL EQE measurement

The device operates as an LED, recorded by an LED photo-luminescence quantum yield measurement system (Enli Tech LQ-100) equipped with a Keithley 2400 Source Measure Unit.

GIWAXS measurement

The measurements were conducted using a Xeuss 2.0 SAXS/WAXS laboratory beamline equipped with a Cu X-ray source (8.05 keV, 1.54 Å) and a Pilatus3R 300K detector. The normal incidence angle was set at 0.3°.

Transient time-resolved microwave conductivity measurement

The perovskite film samples were placed on ETL-coated quartz glasses. These samples were then stimulated using a nanosecond laser pulse, specifically from the LOTIS TII Laser System (LS-2145-OPO). This process generated a specific number of carriers within the samples. Following this, we examined the samples using a microwave. We then monitored the intensity of the reflected microwave as a function of time after photo-excitation, utilizing the Keysight FieldFox spectrum analyzer (N9915A).

Optical Simulations: Optical modeling integrated on the TMM was employed to calculate the optical electric field intensity within all devices. The optical properties of each layer are represented by the index of refraction (η+ iκ) of each material, which was measured using a variable angle spec tropic ellipsometer (VASE). In the calculation, all the simulations of optical properties and exciton generation are based on the assumptions of planar interfaces and isotropy for the layers within the devices. To calculate the exciton generation rate, theoretically, the maximum photocurrent density and loss portion in J_{SC}, 100% IQE, and the AM1.5G intensity spectrum (ASTM G173–03) are assumed.

Other characteristics

SEM was performed on a Crossbeam 540 SEM (Carl Zeiss). Transmission electron microscopy and scanning TEM (HREM) were performed using JEOL JEM-2100F TEM/STEM (Tokyo, Japan) operated at 200 kV. XPS and UPS measurements were performed by the Thermo Fisher Scientific ESCALAB 250Xi system. The measurement of TOF-SIMS was conducted by TOF.SIMS 5-100 (ION-TOF GmbH)

Scanning electron microscopy (SEM) was conducted using a Crossbeam 540 SEM from Carl Zeiss. Transmission electron microscopy (TEM) and scanning TEM (HREM) were performed using a JEOL JEM-2100F TEM/STEM, operated at 200 kV. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) measurements were carried out using the Thermo Fisher Scientific ESCALAB 250Xi system. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) measurements were conducted using the TOF.SIMS 5-100 system from ION-TOF GmbH.

Theoretical calculation

All the calculations are performed in the framework of the density functional theory (DFT) with the projector-augmented plane-wave method, as implemented in the Vienna ab initio simulation package[80]. The generalized gradient approximation proposed by Perdew-Burke-Ernzerhof (PBE) is selected for the exchange-correlation potential[81]. The cut-off energy for plane wave is set to 480 eV. The energy criterion is set to 10^{-5}

eV in the iterative solution of the Kohn-Sham equation. All the structures are relaxed until the residual forces on the atoms have declined to less than 0.02 eV/Å. To avoid interlaminar interactions, a vacuum spacing of 20 Å is applied perpendicular to the slab. The formation energy E_{form} is expressed as

$$E_{form} = E_{defect} - E_{total} - \sum E_{atom} + \sum E_{substituted} + \sum E_{vacancy} \quad (1)$$

where E_{defect} and E_{total} are the energy with and without the defect under the strain of E_{atom}, $E_{substituted}$ and $E_{vacancy}$ are the energy of the added atom, substituted atom and the atom which is supposed to be at the vacancy, respectively.

Data Availability

All data needed to evaluate the conclusions in the paper are present in the paper and/or the supplementary materials and are also available from the corresponding author on reasonable request. Source data are provided with this paper.

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Author Contributions Statement

Conceptualization: G.L., Z. R., and Y. H. Supervision: G.L., Y.Y., and Z. R. Device fabrication: Y. H., J. F., and J. Y. Writing – original draft: Y. H. and Z. R. Writing – discussion, review, editing and finalization: Y. H., Z. R., G. L., and Y. Y. Device characterization and data analysis: Y. H., Z. R., J. F., J. Y., Q. L., Z. X., X. X., D. L.,

R. M., M. C., Y. S., C. Y., J. H., X. C., K. L., P. F., J. H., H. L., Z. L., D. X., L. C., J. Z., G. Y., X. L., Y. Z., Q. T., Q. L., H. H.. Optical simulation: J. Y. All authors participated in the discussion of the results and provided feedback on the manuscript.

Competing Interests Statement: The authors declare that they have no competing interests.

Fig. 1. Properties of acidic M-SQDs with adjustable features and DFT theoretical calculation.

a, High-resolution TEM image of M-SQDs and EDS mapping images from TEM. Inset: electron diffraction pattern of as-prepared M-SQDs. Each green circle represents a single SnO_2 QD. The EDS mapping reveals the element Mg is uniformly distributed in SQDs. **b**, XRD patterns of SQDs powders with varying concentrations of Mg dopants. The vertical red line represents the (110) plane of SnO_2. The phase structure of tetragonal SnO_2 is indexed by the PDF#41-1445. **c**, High-resolution X-ray photoelectron spectroscopy (XPS) spectra of O core levels of intrinsic and Mg-SQDs (O_L: 531.18 eV; O_V: 532.45 eV, O_H: 533.05 eV). XPS characteristic peaks of O 1s can be fitted with three peaks with a mixed Lorentzian/Gaussian line shape and a Shirley background. **d**, Schematic diagram of energy level alignment. The labels of "0.00 M $Mg(Ac)_2$" and "0.01 M $Mg(Ac)_2$" represent the SnO_2 doped without and with 0.01M magnesium acetate tetrahydrate, respectively. **e**, Schematic illustrations of carrier recombination at interfacial contact of ETL and perovskite with a CBO (-) and CBO (+) structure. The blue and red dots represent electrons and holes, respectively. The difference of the work function was represented with black arrows. The blue and red arrows represent the carrier transition path for electrons and holes, respectively. **f**, Local structure and defect formation energy. The blue circle is the position of tin interstitial (Sn_i), and black circle is the position of oxygen vacancy (V_O) defects. (**g**) of intrinsic SnO_2 (color in grayish purple), Mg (substitution)-doped SnO_2 (color in magenta), and Mg (interstitial)-doped SnO_2 (color in purple) with Sn_i or V_O defects.

Fig. 2. Characterizations of $CsPbI_2Br$ perovskite on modulated bottom ETL contacts.

a, ToF-SIMS depth profiles of $CsPbI_2Br$ perovskite on M-SQDs coated FTO substrate. **b**, Time-resolved in situ UV-vis absorption spectra of $CsPbI_2Br$ perovskite crystallization on modulated bottom ETL contacts. **c**, Time-resolved absorbance at the wavelength of 500 nm for samples. **d**, Scanning electron microscopy (SEM), (**e**) PL mapping, and (**f**) GIWAXS patterns of $CsPbI_2Br$ perovskite on SQDs (M-SQDs) coated FTO substrate. **g**, GIWAXS intensity profiles along the q_z direction of the perovskite films. **h**, The intensity azimuthal pole (**f**) along the (110) plane. The (110) planes were fitted with Gaussian distribution method.

Fig. 3. Depth-profiling GIWAXS characterization on the degradation pathway of the $CsPbI_2Br$ perovskite.

(a, c, e) GIWAXS patterns of fresh and aged $CsPbI_2Br$ perovskite on Com-SnO_2 contact (pH~11) substrates with incident angles of 0.2°, 0.4° and 1°, respectively. (b, d, f) GIWAXS patterns of fresh and aged $CsPbI_2Br$ perovskite on M-SQDs-based contact (pH~1) substrates with incident angles of 0.2°, 0.4°, and 1°, respectively. Mechanism of degradation of perovskite films prepared with alkaline (g) and acidic (h) substrates in a highly humid environment. The gray arrow represents the distortion of the lattice under high humidity environment. The water vapor adsorbed on the surface of inorganic perovskites can trigger the $\alpha \rightarrow \delta$ phase transition. The arrow with wathet blue shows the path in which water molecules penetrate through grain boundaries. The blue arrow displays the movement path of OH^- in alkaline substrate in humid environment, which interact with Pb^{2+} and damage the perovskite lattice. The red cross indicates that the acidic substrate inhibits the formation of OH^- species in humid environment.

Fig. 4. Photovoltaic performance of single junction $CsPbI_2Br$ PSCs and OSCs.

a, *J-V* curves and (**b**) PCE statistic of the Com-SnO_2, SQDs, and M-SQDs based devices. 20 cells of each set of solar cells were measured. The boxes indicate 25th (upper quartile) to 75th (lower quartile) percentiles. **c**, The steady-state PCE under maximum power point (MPP) and stabilized J_{SC} for 500s. **d**, EQE curve of M-SQDs based PSC. **e**, EQE of electroluminescence for the devices. The 'X' symbols marked the EQE_{EL} at the injection current density equal to J_{SC}. **f**, Comparison of V_{OC} with WBGs reported in the literature[12,16,20,51,52,53,54,55,56,57,58,59,60,61,62,63,64,65,66,67,68,69,70,71,72,73,74,75,76,77] (yellow circle) and this work (red star) (All photovoltaic parameters are provided in Supplementary Table 8). The '70%', '80%' and '90%' lines represent the 70%, 80%, and 90% of DB-limit, respectively. **g**, Schematic diagram of OSC device structure and chemical structures of active materials. J-V curve (**h**) and EQE curve (**i**) of OSC with a n-i-p architecture.

Fig. 5. Photovoltaic performance of monolithic all-inorganic Perovskite/Organic TSCs.

a, Schematic diagram of tandem device structure and SEM cross-sectional image of perovskite/organic tandem device. **b**, J-V curves of M-SQDs-based tandem devices. **c**, EQE curves of PSC and OSC within POTSCs. **d**, Steady power output tracking of the devices with continuous one-sun illumination at a maximum power point (MPP). The initial efficiency of the encapsulated tandem cell prepared with Com-SnO_2, SQDs and M-SQDs was 20.42%, 21.85%, and 24.51%, respectively. **e**, Normalized PCEs of TSCs based on com-SnO_2, SQDs, and M-SQDs during temperature cycle tests from -40°C to 85°C. Initial PCEs for encapsulated TSCs based on com-SnO_2, SQDs, and M-SQDs were 20.56±0.5%, 23.11±0.3%, and 24.11±0.25%, respectively. 3 cells of each set of solar cells were measured. The error bars in (e) represent the standard deviation (SD) among PSCs. The dashed horizontal lines represent 40%, 60%, 80% of the initial performance of the devices.

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