

Thermionic Emission–Based Interconnecting Layer Featuring Solvent Resistance for Monolithic Tandem Solar Cells with Solution-Processed Perovskites

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All-perovskite tandem cells have been considered a potential candidate for bringing the power conversion efficiency (PCE) beyond the Shockley–Queisser limit of single-junction device while retaining the advantages of earth-abundant materials and solution processability. However, a challenging issue with regard to realizing such solution-processed devices is the fulfillment of complex and coupled requirements of the interconnecting layer (ICL), including solvent resistance to protect underlying perovskite film, high electrical properties for carrier transport and recombination, and high optical transmission. In this work, a new thermionic emission–based ICL with enhanced solvent resistance features is demonstrated. Fundamentally, the thermionic emission plays a critical role in the electron transport process in the ICL, which is confirmed through both experimental and theoretical studies. Besides achieving high optical transmission and electrical properties, the new ICL chemically protects the underlying perovskite film by introducing a fluoride silane–incorporated polyethylenimine ethoxylated hybrid system that also passivates the surface defects to reduce electrical loss. The monolithic all-perovskite tandem cells demonstrate highest PCE of 17.9% (from current density–voltage scan) and the highest steady-state efficiency is 16.1% for a typical device. Consequently, this work contributes to not only understanding the fundamental mechanism of ICLs but also promotes robust and low-cost photovoltaics.

22.7%,^[1] while theoretical studies predict PCE limit toward 31%.^[2,3] In addition, perovskite materials possess the interesting features of high absorption coefficient, long carrier diffusion length, sharp absorption cutoff, tunable bandgap, and simple fabrication processes.^[4–10] Although various perovskite single-junction solar cells have been investigated,^[11–17] their PCEs are ultimately limited by the Shockley–Queisser limit, because the single-junction cells typically cannot utilize photons with energies less than the bandgap of perovskite active layer and thermalization losses occur at high photon energy. To overcome the fundamental limit of single-junction efficiency, developing tandem solar cells is a valid strategy for improving the light-harvesting efficiency for both short- and long-wavelength photons.

Tandem solar cells of perovskite film integrated with conventional photovoltaic techniques, such as silicon solar cells,^[18–20] copper indium gallium selenide (CIGS) solar cells,^[21,22] and organic solar cells,^[23–25] have been widely reported implying the

prominent potential of perovskite materials in tandem application. Notably, perovskite materials are ideal candidates as the light absorbers in tandem solar cells. The bandgap of perovskite varies from 1.2 to 2.2 eV, which is easily tunable by modifying the chemical composition of perovskite.^[26,27] In addition, the easy-fabrication methods of perovskite films, including solution process, printing, and vacuum deposition,^[28,29] are more feasible and relaxed compared with conventional semiconductor fabrication process. Together with the interesting features of high absorption coefficient, solution processability, and low cost, it is highly desirable to realize all-perovskite tandem solar cells.^[30–32] The PCE of monolithic all-perovskite tandem cells is predicted to surpass that of perovskite single-junction devices by 2020.^[33]

It is still a challenge to develop tandem cells with solution-processed perovskites owing to the lack of robust interconnecting layers (ICLs). In such tandem cells, the ICL should simultaneously achieve complex and coupled properties, including 1) high electrical properties for efficient carrier transport and recombination, 2) high optical transmission minimizing optical loss, and

1. Introduction

Organohalide perovskite solar cells have attracted extensive attention recently due to their extremely rapid development. The certified power conversion efficiency (PCE) has achieved

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3) solvent-resistant function to protect the underlying perovskite film from the solvent of the upper perovskite, which is significantly important in monolithic all-perovskite tandem cells. From the literature, the investigations of monolithic all-perovskite tandem solar cells with solution-processed absorbers are limited. Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) film was employed as the recombination layer by dry transfer process in a monolithic $\text{CH}_3\text{NH}_3\text{PbI}_3\text{-CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI₃-MAPbI₃) tandem solar cell.^[34] While the device fabrication process only involved dry transfer and solution process, the PCE was limited by the low electrical property of the ICL and nonoptimized light absorption range. Besides, solution-processed two-terminal perovskite-perovskite tandem solar cell utilizing sputtered indium tin oxide (ITO) as the recombination layer (RL) in the ICL structure has achieved PCEs of 17%^[35] and 18.4%.^[36] ITO made by sputtering can act as a good RL in the ICL structure for achieving high tandem performance with good solvent resistance, electrical conductivity, and optical transmission. However, regarding costly rare metal and brittle issues of ITO, further efforts are necessary to investigate alternative ICLs for future applications.

In this work, a new thermionic emission-based ICL structure is demonstrated for highly efficient all-perovskite tandem cells. The complementary wide- and narrow-bandgap perovskite films in this tandem cell are both fabricated by solution process. Fundamentally, the thermionic emission-assisted electron transport mechanism of this new ICL is confirmed both experimentally and theoretically, which facilitates efficient electron transport from the subcell to the ICL and enhances tandem cell performance. Besides achieving the high optical transmission properties, the new ICL fulfills the complex and coupled requirements of good solvent resistance and high electrical properties. A new fluoride silane-incorporated polyethylenimine ethoxylated hybrid system, hereafter named as FSIP hybrid system, is proposed and introduced into our ICL. This novel FSIP hybrid system offers dual functions of enhancing solvent resistance to protect the underneath perovskite layer and passivating perovskite defects to suppress the nonradiative recombination leading to considerable enhanced electrical properties. With the optimized ICL structure composed of FSIP/C₆₀/bathocuproine (BCP)/ultrathin Cu:Au alloy/PEDOT:PSS, the tandem cells exhibited high PCE up to 17.9% with negligible hysteresis. To our knowledge, this is the highest efficiency in monolithic all-perovskite tandem solar cells with solution-processed perovskites and indium-free ICLs. This work not only contributes to the fundamental understanding of ICL electrical properties but also promotes the evolution of robust and low-cost monolithic all-perovskite tandem solar cells with high performances for promoting the application of perovskite photovoltaics.

2. Results and Discussion

2.1. Solvent Resistance of FSIP Hybrid System Preventing Aqueous Solvent Damage

The proposed ICL structure consists of four layers: a dual-functional FSIP hybrid system, an electron transport layer (ETL) of C₆₀/BCP, an RL of ultrathin transparent metal alloy (Cu/Au),

and a hole transport layer (HTL) of PEDOT:PSS. The FSIP hybrid system is the most important component in the ICL offering solvent resistance for the perovskite film. Silane materials with hydrophobic functional groups have previously been employed to modify perovskite surface for improving stability under moisture.^[37–40] However, the solvent-resistant effect and electron transport mechanism of these materials in the ICL of perovskite tandem cell are still not clear. Differently, for the first time, we demonstrate that a dual-functional FSIP hybrid system in the ICL of solution-processed all-perovskite tandem cell offers effective protection for the underlying perovskite layer by solvent resistance against aqueous solution for maintaining its good morphology as well as optical and electrical properties, resulting in very high tandem cell efficiency. Simultaneously, the FSIP hybrid system can passivate perovskite defects to reduce the nonradiative recombination at the perovskite/ETL interface contributing to V_{OC} and PCE improvement of perovskite solar cells as described in the next section.

The new FSIP hybrid system is composed of fluoride silane and polyethylenimine ethoxylated (PEIE) in which trichloro(3,3,3-trifluoropropyl)silane (FPTS) is proposed as a silanizing agent incorporated on PEIE. The chemical structures of FPTS and PEIE are shown in **Figure 1**. Regarding the unique dual-functional FSIP hybrid system, it prevents aqueous solvent damage from the spin coating of PEDOT:PSS in the subsequent steps for forming the HTL. The effect of the FSIP hybrid system was first verified by visual examination of perovskite films (with and without FSIP hybrid system) after the spin coating of PEDOT:PSS solution. As shown in Figure S1 in the Supporting Information, after spin coating aqueous-based PEDOT:PSS, the perovskite film without the FSIP hybrid system is damaged by water, while the perovskite film protected by FSIP shows no clear damage and good film morphology.

For realizing and understanding the FSIP hybrid system, we start with bare PEIE, which is hydrophilic and is confirmed by its initial dispersion in water. To avoid aqueous solvent damage from the subsequent spin coating of PEDOT:PSS, the interface of PEIE/perovskite should be converted to hydrophobic. Silanization is a process known to increase surface hydrophobicity. As a silanizing agent, FPTS with hydrophobic functional groups is introduced to form the hybrid system with PEIE on perovskite surface by crosslinking and hydrogen bonding. Using a low-temperature chemical vapor deposition treatment process (detailed in the Experimental Section), the FPTS molecules crosslinked with each other by silane coupling process and the hydroxyls on the PEIE formed hydrogen bonds with FPTS. To confirm the existence and crosslinking of FPTS, attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy has been performed. Figure 1(c) shows the ATR-FTIR spectra of bare perovskite film, PEIE-coated perovskite film, and FSIP-coated perovskite film. Because of the existence of ammonium groups in perovskite film, it is difficult to distinguish the feature bands of PEIE from that of the perovskite film. Compared with the spectra of bare perovskite film, the new bands at 1233 and 1030 cm^{-1} in the spectra of PEIE-coated perovskite are assigned to hydroxyl group deformation vibration and C–O vibration, respectively, revealing the existence of PEIE on perovskite film. Furthermore, after the FPTS treatment, there are some new bands clearly shown in the FTIR spectra compared with the

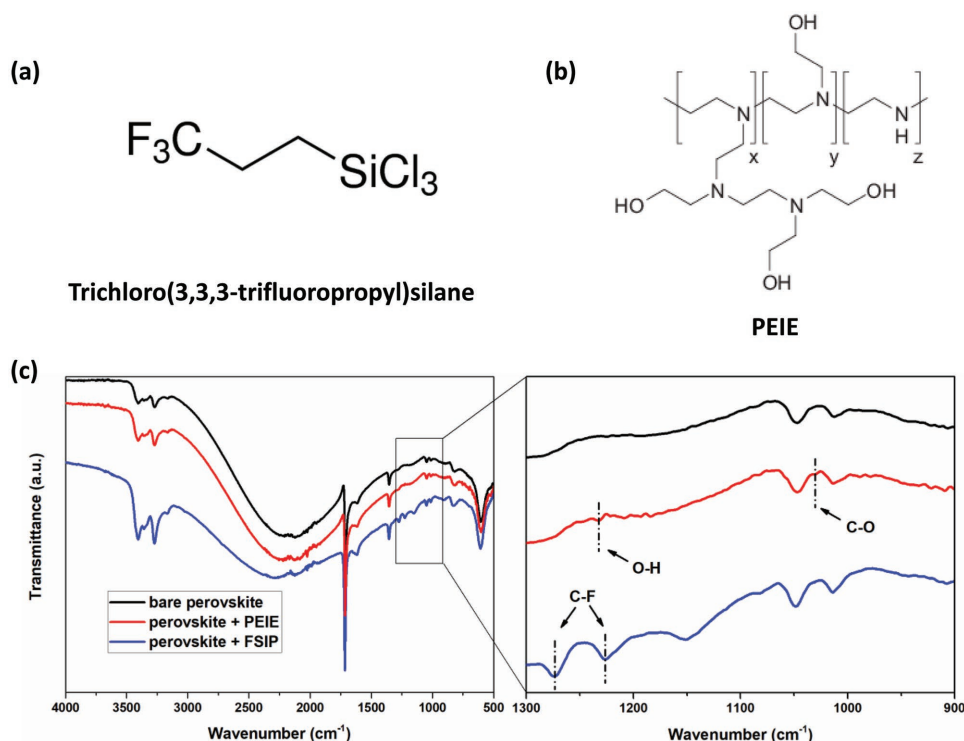


Figure 1. Chemical structures of a) FPTS and b) PEIE. c) ATR-FTIR spectra of bare perovskite film, PEIE-coated perovskite film (perovskite + PEIE), and FSIP-coated perovskite film (perovskite + FSIP).

as-prepared PEIE-coated perovskite film. The vibration bands at 1274 and 1226 cm^{-1} are assigned to $-\text{CF}_3$ groups^[37] showing the existence of molecular FPTS on PEIE film. The Si—O—Si bands are in the range of 1200–1000 cm^{-1} , which is obscured by the perovskite bands. To further investigate the interaction of PEIE and FPTS, the FTIR spectra of PEIE and FSIP hybrid system are shown in Figure S2 in the Supporting Information. The vibration bands at 1021 and 1126 cm^{-1} in FSIP hybrid system are ascribed to Si—O—Si groups,^[41] which confirmed the crosslinking between FPTS molecules by forming Si—O—Si groups. Hydrogen bonds between molecular FPTS and PEIE film cannot be directly observed in the FTIR spectra but it would affect C—O bands. The vibration band of C—O in PEIE is at 1074 cm^{-1} and it shifts to a lower frequency of 1069 cm^{-1} when hydrogen bonds are formed with the molecular FPTS.

To further confirm the existence of FPTS and investigate the hydrophobicity of the perovskite/PEIE surface, water contact angle characterization was carried out. **Figure 2** shows the water contact angles of perovskite films after different treatments. For bare perovskite, because of the intrinsic hydrophilic property, a small contact angle of only 54.1° was observed in **Figure 2(a)**, which is consistent with others.^[38,42] As shown in **Figure 2(b)**, the contact angle of perovskite/PEIE (0.01 wt%) further decreased from 54.1° to 51.6°, suggesting that PEIE introduces hydroxyl groups causing the slightly more hydrophilicity of the perovskite film. Differently, the addition of FPTS into the FSIP hybrid system attaches hydrophobic functional groups to the surface, which considerably increases the contact angle to 75.6° (see **Figure 2(c)**). Importantly, rather than increasing the concentration of FPTS, the increase of PEIE

concentration (from 0.01 to 0.05 wt%) resulted in enhanced surface hydrophobicity, as indicated by an even larger contact angle of 92.5° in **Figure 2(d)**. The increased hydrophobicity at higher PEIE concentration in the presence of FPTS can be understood as the PEIE on the perovskite film providing more sites for the silanization process leading to a higher coverage of the hydrophobic FSIP hybrid system. Consequently, the FPTS crosslinked with each other and formed hydrogen bonds with PEIE to achieve the novel FSIP hybrid system, which highly enhanced the perovskite surface hydrophobicity and enabled solvent-resistant function.

2.2. Defect Passivation of FSIP Hybrid System

Besides protecting the bottom perovskite layer from solvent damage by solvent-resistant property, the FSIP hybrid system in our ICL can significantly enhance electrical properties of the solar cells. To closely investigate the influences of the FSIP hybrid system, single-junction MAPbI_3 solar cell with the structure of $\text{ITO}/\text{NiO}_x/\text{MAPbI}_3/\text{FSIP}/\text{C}_{60}/\text{BCP}/\text{Ag}$ was constructed compared to the reference of $\text{ITO}/\text{NiO}_x/\text{MAPbI}_3/\text{C}_{60}/\text{BCP}/\text{Ag}$. The PEIE concentration in the FSIP hybrid system is first optimized. When a PEIE concentration of 0.05 wt% is used, the device is almost open circuit with very low current density. Therefore, the PEIE concentration used in FSIP hybrid system is subsequently lowered to 0.01 wt%. **Figure 3** shows the solar cell parameters without and with the FSIP hybrid system. By inserting a FSIP hybrid system into the single-junction cells, the average PCE considerably improves from 9.39% to 10.3%.

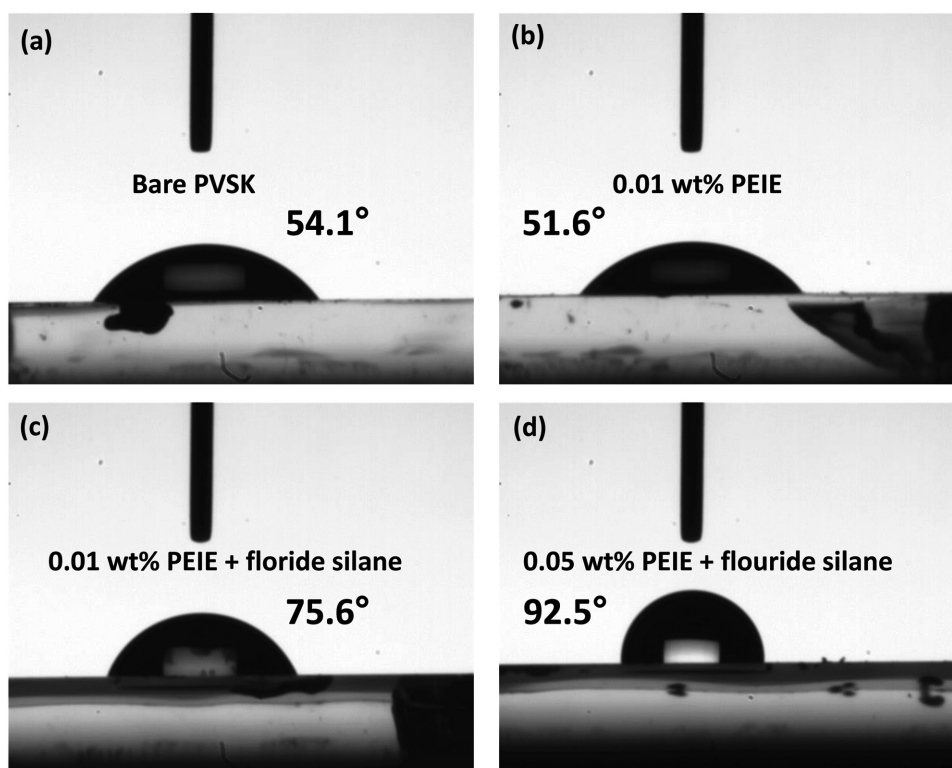


Figure 2. Water contact angles of a) bare perovskite (PVSK) film, b) perovskite/PEIE (PEIE concentration 0.01 wt%), c) perovskite/FSIP (PEIE concentration 0.01 wt%), and d) perovskite/FSIP (PEIE concentration 0.05 wt%).

Figure 3(b)–(d) shows the influences of FSIP hybrid system on V_{OC} , fill factor (FF), and short-circuit current density (J_{SC}), respectively. It is found that the PCE increment mainly comes from higher V_{OC} and FF, with V_{OC} of the FSIP cell improved from 0.99 to 1.05 V and FF from 0.73 to 0.77. Regarding J_{SC} , the average J_{SC} only slightly decreases from 12.91 to 12.71 mA cm^{-2} by a very small percentage of 1.5%, which is almost negligible. The improvement of FF and V_{OC} in the single-junction solar cells indicates enhanced electrical properties introduced by the FSIP hybrid system.

To study the origin of the electrical enhancement by using the FSIP hybrid system, photoluminescence (PL) measurement was further conducted. As shown in Figure S3(a) in the Supporting Information, the PL peak of perovskite film with C_{60} /BCP is around 760 nm. After the insertion of the FSIP hybrid system, the PL peak shifts to 740 nm. The blue shift of the perovskite PL peak (≈ 20 nm) indicates the surface defect passivation in the perovskite film, as stated by others.^[43] To further confirm the electrical enhancement effect, time-resolved photoluminescence was carried out. As shown in Figure S3(b) in the Supporting Information, the lifetime considerably prolongs from 0.44 ns for $\text{MAPbI}_3/\text{C}_{60}/\text{BCP}$ to 3.95 ns for $\text{MAPbI}_3/\text{FSIP}/\text{C}_{60}/\text{BCP}$. The longer lifetime indicates that the FSIP hybrid system can effectively reduce the surface defect concentration in the perovskite film, which suppresses the nonradiative recombination at the perovskite/ETL interface leading to enhanced electrical properties. To prove the defect passivation effect, space-charge-limited current is used to characterize the defect density of MAPbI_3 film with or without FSIP hybrid

system. The extracted defect density decreases from 6.37×10^{16} to $2.77 \times 10^{16} \text{ cm}^{-3}$ after the insertion of FSIP hybrid system, as shown in Figure S3(c) and (d) in the Supporting Information. Consequently, the unique FSIP hybrid system in our ICL combining FPTS and PEIE offers dual functions of solvent resistance and defect passivation in solution-processed perovskite solar cells, which 1) prevent the polar solvents' penetration to protect the bottom perovskite film against the aqueous solvent of PEDOT:PSS by improving its surface hydrophobicity, and 2) simultaneously passivate the surface defects of the perovskite film and reduce the nonradiative recombination, which enhances the electrical properties of the solar cells.

2.3. Working Mechanisms of the Thermionic Emission–Based ICL

The electrical properties of the ICL ($\text{FSIP}/\text{C}_{60}/\text{BCP}/\text{metal(s)}/\text{PEDOT:PSS}$) with the wide-bandgap ($\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.5}\text{I}_{0.5})_3$) and narrow-bandgap ($\text{FA}_{0.5}\text{MA}_{0.5}\text{Pb}_{0.5}\text{Sn}_{0.5}\text{I}_3$) perovskite materials used in the all-perovskite tandem cells (details described in the next section) are theoretically and experimentally investigated. While the carrier transport properties of C_{60} and PEDOT:PSS^[11,35,36] and the carrier recombination property of the metal layer^[24,44] have been reported, it is necessary to unveil the role of the interlayers of FSIP hybrid system and BCP in detail for understanding the working mechanism of the new multilayered ICL structure. Theoretically, a drift–diffusion-based carrier transport model is introduced to study the electrical properties of the ICL as described in the

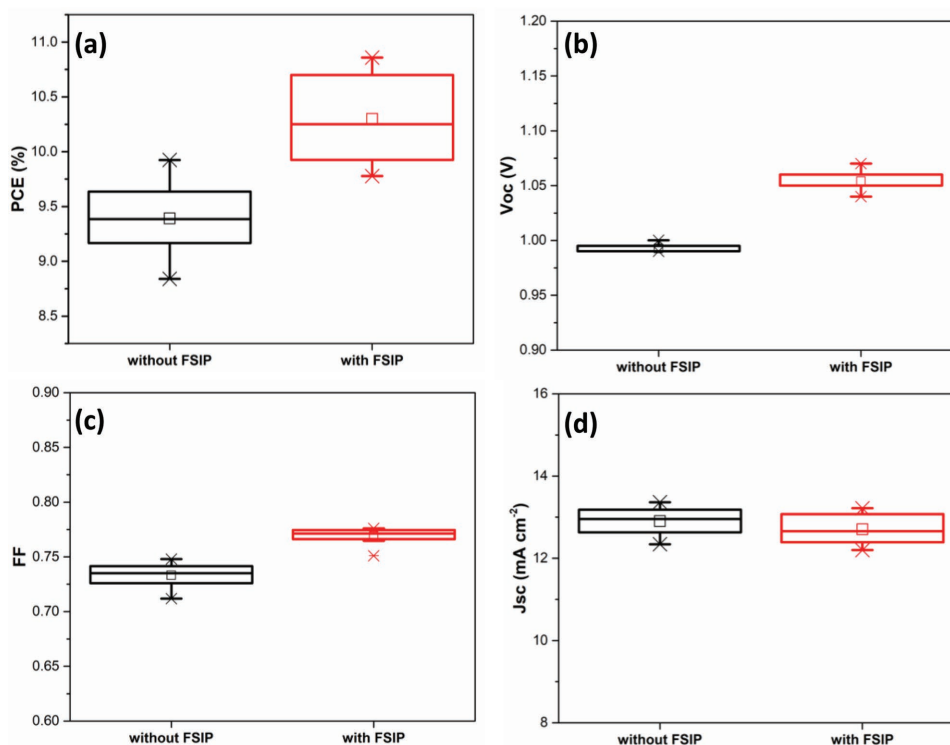


Figure 3. Current density–voltage (J – V) curve parameters under AM1.5G illumination with distribution statistics of a) PCE, b) V_{OC} , c) FF, and d) J_{SC} for MAPbI₃ single-junction solar cells without and with FSIP.

Experimental Section. The J – V characteristics of various single-junction perovskite solar cells with and without FSIP hybrid system in device structures of ITO/NiO_x/wide-bandgap perovskite/FSIP/C₆₀/Ag and the tandem solar cells at different temperatures from 240 to 300 K were experimentally investigated. Besides FSIP hybrid system, we also studied the J – V characteristics of perovskite solar cells with or without BCP for the full picture of the thermionic emission–governed features of the ICL.

In the theoretical modeling, based on the physical properties discussed in the previous sections, the FSIP hybrid system is regarded as an ultrathin insulating layer (≈ 5 nm) with a very high conduction band and low valance band. While the hole transport is blocked by the low valance band of the FSIP hybrid system, in order to accurately simulate the device physics of the interlayer, electron transport through the FSIP hybrid system is studied by the revised thermionic-field-emission (TFE) theory that includes both thermionic emission and quantum tunneling.^[45] In this theory, the electron transport toward the insulating layer will surmount the barrier with the help of thermal energy (by thermionic emission) and the electric field (by quantum tunneling). The electron current in the FSIP hybrid system region is given by the equation

$$J_n = q \left(v_n^r n^r - v_n^l n^l \exp \left(\frac{-\Delta E_C}{k_B T} \right) \right) + J_{ntun} \quad (1)$$

where n^r and n^l , respectively, are the electron densities at the right- and left-hand sides of the interfaces between the FSIP hybrid system and the adjacent layers, and v_n^r and v_n^l ,

respectively, are the electron thermal velocities at the right- and left-hand sides of the interfaces, which are quadratic functions of temperature. ΔE_C is the energy change of the conduction band. Apart from the thermionic emission part, J_{ntun} referring to the quantum tunneling electron current has also been determined by Equation (S5) in the Supporting Information. Overall, the electron transport through the FSIP hybrid system taking into account the thermionic emission and the quantum tunneling has been studied.

The experimental and modeled room-temperature J – V characteristics of the wide-bandgap perovskite single-junction cells with or without FSIP hybrid system are shown in **Figure 4(a)**, and the temperature-dependent J – V characteristics of devices with and without FSIP are shown in **Figure 4(b)** and **Figure S5(a)** in the Supporting Information, respectively. It is observed that devices with FSIP hybrid system have much larger FF and V_{OC} . This result indicates that the FSIP hybrid system can optimize the carrier transport inside the device, and also reduce the electrical loss due to defect passivation. Besides, taking the FSIP hybrid system into consideration, the theoretical results shown in **Figure 4(a)** give an identical discrepancy between the groups with or without FSIP, which matches the experimental results well. From the theoretical and experimental results, it is clear that the FSIP hybrid system is beneficial to the performance of the device, but the detailed electron transport mechanism of this layer still needs further study under different temperatures.

When the temperature is less than 300 K, obvious S-shape J – V curves appear (see in **Figure 4(b)** and **Figure S5(a)** in the Supporting Information) indicating that new obstacles

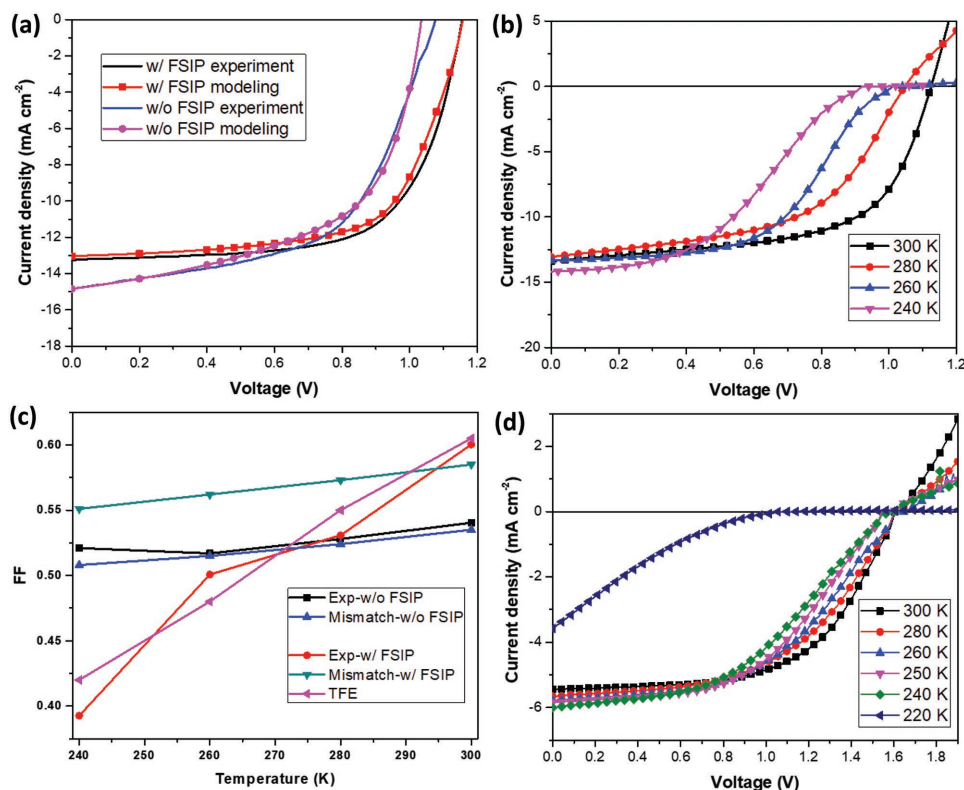


Figure 4. a) Experimental and modeled room-temperature J - V characteristics of the single-cell device of wide-bandgap (FA_{0.83}Cs_{0.17}Pb(Br_{0.5}I_{0.5})₃) perovskite with or without FSIP hybrid system. b) J - V characteristics of wide-bandgap (FA_{0.83}Cs_{0.17}Pb(Br_{0.5}I_{0.5})₃) perovskite single cells with FSIP hybrid system under temperatures from 240 to 300 K. c) FFs of single cells with or without the interlayer at different temperatures. The curves "Exp," "Mismatch," and "TFE" refer to the experimental FF, the theoretical FF changed due to energy band mismatch, and theoretical FF changed due to thermionic field emission, respectively. d) J - V characteristics of the all-perovskite (wide (FA_{0.83}Cs_{0.17}Pb(Br_{0.5}I_{0.5})₃) and narrow (FA_{0.5}MA_{0.5}Pb_{0.5}Sn_{0.5}I₃)) tandem solar cells with FSIP and BCP in ICL at temperatures from 220 to 300 K.

to electron transport are formed.^[46] In order to facilitate the theoretical and experimental analyses of the carrier transport changes, FF is extracted from J - V curves at different temperatures, as shown in Figure 4(c). Significant changes of FF in experiments are observed. From 240 to 300 K, the FF increased from 0.52 to 0.54 for the device without FSIP hybrid system, while the increase for the device with FSIP hybrid system is much larger (from 0.39 to 0.60). Since FF reflects the balance between the carrier generation by the active layer and extraction by the electrodes, the discrepancy in the changes of FF depending on the temperature reveals that the electron transport process with the FSIP hybrid system is much more sensitive to the temperature. Together with the experimental results, the fundamental mechanism of the electron transport through FSIP hybrid system can be further unveiled as below.

The effects of several temperature-dependent physical mechanisms on solar cell performances are explored, in which the significant FF changes upon the temperature are mainly contributed by the two aspects: 1) carrier accumulation by the energy band mismatch and 2) and the TFE of the FSIP hybrid system. It should be noted that, although the bulk Shockley-Read-Hall (SRH) recombination rate in perovskite active layer is also sensitive to the temperature as expressed by Equation (S4) in the Supporting Information, the effect from the bulk SRH

recombination is relatively weak compared to those effects ascribed to the energy band mismatch and the TFE of the FSIP hybrid system; therefore, it is not included in the analysis. The temperature-dependent FFs influenced by different physical causes in the device simulation with and without the FSIP hybrid system are calculated, as shown in Figure 4(c). Importantly, the energy band mismatch between the active layer and carrier transport layers will form barriers for carrier transport, which results in carrier accumulation and extra surface recombination loss, thus greatly reducing the FF. As temperature increases from 240 to 300 K, more carriers are extracted and thus the carrier accumulation reduces, implying FF increases. Our theoretical results show that FF changes in the device without FSIP hybrid system are mainly attributed to energy band mismatch (see "Mismatch-w/o FSIP" in Figure 4(c)). However, in the devices with FSIP hybrid system, if we only consider energy band mismatch and the TFE current boundary condition for FSIP hybrid system is temporarily removed (the conduction band of FSIP hybrid system is also pinned to that of C₆₀ to avoid unnecessary disturbance), the much larger FF increase from 240 to 300 K cannot be simply explained by the effect of energy band mismatch alone (as indicated by the "Mismatch-w/ FSIP" curve in Figure 4(c)). Interestingly, when the TFE theory is included in the modeling, the experimental results, particularly the temperature dependence of FF in the

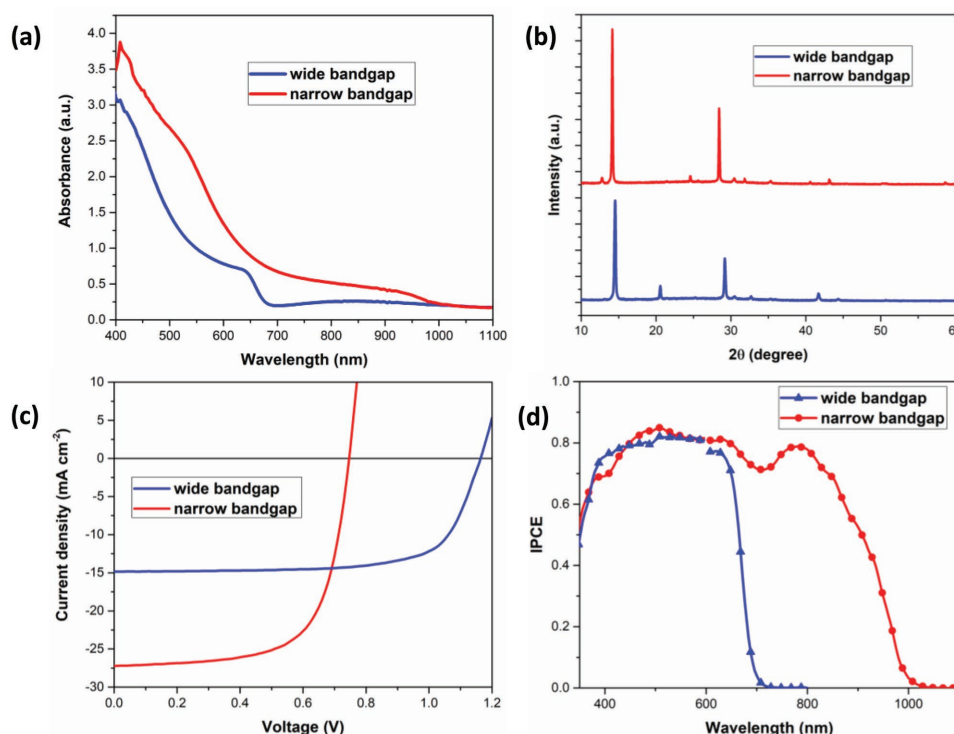


Figure 5. a) Absorbance and (b) XRD spectra of wide-bandgap and narrow-bandgap perovskite film on glass, c) light J - V curves under AM1.5G illumination, and d) IPCE of wide-bandgap and narrow-bandgap perovskite single-junction solar cells.

FSIP device, can be well described by our modeling results (see “Exp-w/ FSIP” and “TFE” curves in Figure 4(c)). Therefore, the numerical and experimental results confirm that the efficient electron transport through the FSIP hybrid system is highly temperature dependent and should be attributed to a thermionic-field-emission transport process. However, the tunneling process is only slightly affected by the temperature, which implies that the tunneling part has minor effect in our study. Overall, the electron transport through the FSIP hybrid system is mainly thermionic emission-based transport process.

Similar low-temperature discussion and modeling are also applicable to solar cells with BCP layer (see Figures S6 and S7 in the Supporting Information), which indicates thermionic emission is also important for the BCP layer. The temperature-dependent J - V curves of all-perovskite tandem solar cells are shown in Figure 4(d). The similar S-shape J - V curves at lower temperature show the significant influence of the thermionic emission of FSIP hybrid system and BCP layers in the ICL system. Consequently, the thermionic emission-based ICL can promote efficient electron transport from the subcell to the RL of Cu/Au metal electrode and facilitate carrier recombination at RL for achieving a higher performance in perovskite tandem solar cells.

2.4. Highly Efficient Monolithic All-Perovskite Tandem Solar Cells

In monolithic all-perovskite tandem solar cells, the bandgap of two absorbers should be optimized for extending the absorption range and obtaining the highest performance.

According to theoretical calculations, the bandgap of the wide-bandgap perovskite subcell should be 1.8 eV, and that of the narrow-bandgap subcell should be around 1.2 eV.^[35] One important advantage of all-perovskite tandem solar cells is that the perovskite bandgap could be easily tuned by different doping. By replacing parts of I atoms with Br atoms, the perovskite bandgap would increase.^[47] While substituting some Pb atoms with Sn atoms, the perovskite bandgap would decrease accordingly.^[48,49] Here we modified the wide-bandgap film fabrication process taking into account the information from the reported literature.^[35] The wide-bandgap perovskite was $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.5}\text{I}_{0.5})_3$ with an absorption edge around 690 nm, corresponding to 1.83 eV bandgap, as shown in Figure 5(a). The narrow-bandgap solar cell was modified based on our previous publication.^[50] To improve the stability and optimize the bandgap, the narrow-bandgap perovskite was chosen to be $\text{FA}_{0.5}\text{MA}_{0.5}\text{Pb}_{0.5}\text{Sn}_{0.5}\text{I}_3$ with an absorption edge around 1000 nm, corresponding to 1.24 eV bandgap, as shown in Figure 5(a). The wide-bandgap film mainly absorbed photons with wavelength between 300 and 690 nm. The remaining photons would transmit through the ICL layer and then be absorbed by the narrow-bandgap film. Figure 5(b) shows the X-ray diffraction (XRD) spectra of the wide-bandgap and narrow-bandgap perovskite films, which confirmed that the two perovskites had good film qualities. Figure 5(c) shows the current density-voltage (J - V) curves of the wide-bandgap single-junction solar cell (with FSIP) and the narrow-bandgap single-junction solar cell. The wide-bandgap single-junction solar cell exhibited a V_{OC} of 1.16 V, J_{SC} of 14.84 mA cm⁻², and FF of 0.72, giving a PCE

Table 1. J - V curve parameters of wide-bandgap and narrow-bandgap single-junction solar cells under AM1.5G illumination.

	J_{SC} [mA cm ⁻²]	V_{OC} [V]	FF	PCE [%]
Wide-bandgap solar cell	14.68 ± 0.39	1.15 ± 0.01	0.73 ± 0.04	12.29 ± 0.41
Narrow-bandgap solar cell	27.40 ± 0.55	0.75 ± 0.01	0.65 ± 0.02	13.40 ± 0.46

of 12.32%. The corresponding incident photon-to-current efficiency (IPCE) is shown in Figure 5(d) with an integrated J_{SC} of 14.35 mA cm⁻² (within a reasonable 3.57% error vs the actual J_{SC}). For the narrow-bandgap single-junction solar cell, the V_{OC} , J_{SC} , and FF are 0.75 V, 27.24 mA cm⁻², and 0.67, respectively, resulting in a PCE of 13.61%. The integrated J_{SC} from the IPCE (shown in Figure 5(d)) of the narrow-bandgap single-junction solar cell is 26.69 mA cm⁻² (within a reasonable 2.02% error vs the actual J_{SC}). The average photovoltaic parameters are summarized in Table 1.

The structure of the monolithic all-perovskite tandem solar cells using the proposed ICL was ITO/NiO_x/wide-bandgap subcell/FSIP/C₆₀/BCP/Cu/Au/PEDOT:PSS/narrow-bandgap subcell/polystyrene/C₆₀/BCP/Ag, as shown in Figure 6(a). Here the total thickness of our ICL was selected to be around 100 nm, which can prevent the penetration of perovskite solvents such as γ -butyrolactone and dimethyl sulfoxide. It is worth noting that the overall ICL fabrication is indium-free and only involved solution process and thermal evaporation.

The J - V characteristic of a typical tandem solar cell (under forward and reverse scanning) is given in Figure 6(b), which shows a V_{OC} of 1.72 V, J_{SC} of 12.80 mA cm⁻², and FF of 0.73 resulting in a high PCE of 16.07%. To characterize the hysteresis feature of perovskite solar cell, a modified hysteresis index as defined by Kim and Park^[51] is used to quantitatively describe the hysteresis. For our tandem solar cell, the hysteresis index is lower than 0.05 (only 0.034) indicating that the

Table 2. Summarized J - V curve parameters of tandem devices under AM1.5G illumination. The average value and the standard deviation were obtained from 18 devices.

	J_{SC} [mA cm ⁻²]	V_{OC} [V]	FF	PCE [%]
Forward scan	12.62 ± 0.32	1.74 ± 0.04	0.69 ± 0.03	15.11 ± 0.98
Reverse scan	12.55 ± 0.33	1.73 ± 0.04	0.68 ± 0.03	14.79 ± 1.06

hysteresis in our tandem cell was negligible.^[52] The stabilized power output (SPO) at maximum power point of the tandem cell is shown in Figure 6(c). After stabilization, the PCE was slightly more than 16.10%, which may come from light soaking. Unlike four-terminal tandem solar cells, in which two subcells work independently, monolithic tandem solar cells require current matching. The IPCEs of individual subcells are shown in Figure 6(d), indicating that the current matching requirement is fulfilled in the tandem solar cell. The integrated J_{SC} values of each subcell are very close to the measured J_{SC} values in the J - V curve of the tandem cell. The average J - V parameters of our tandem solar cells are summarized in Table 2. For the forward scanning, the average V_{OC} , J_{SC} , and FF are 1.74 V, 12.62 mA cm⁻², and 0.69, respectively, with the average PCE being 15.11%. For the reverse scanning, the average V_{OC} , J_{SC} , and FF are 1.73 V, 12.55 mA cm⁻², and 0.68, respectively, with the average PCE being 14.79%. The average V_{OC} obtained from tandem cell is very close to the sum of individual subcells. The highest PCE of our all-perovskite tandem solar cells was 17.90% (J - V curve, photovoltaic parameter, and IPCE of the best-performance cell are summarized in Figure S8 in the Supporting Information). The tandem devices in this work show the highest performance (in terms of both the average and highest PCEs) among reported monolithic all-perovskite tandem solar cells with solution-processed perovskites and indium-free ICL.

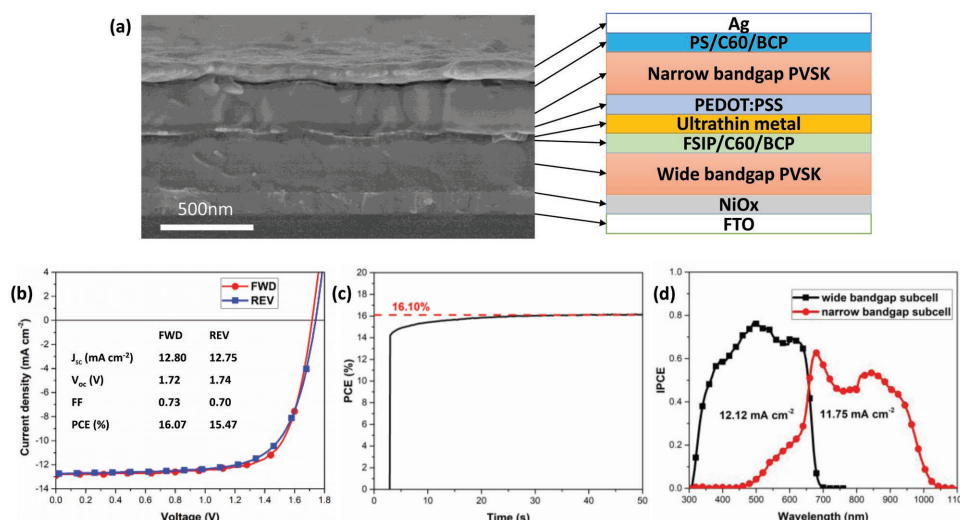


Figure 6. a) Cross-view scanning electron microscope images of monolithic all-perovskite (PVSK) tandem solar cell structure and cell schematic, b) light J - V curve of tandem device with forward (from short circuit to open circuit) scanning (FWD) and reverse (from open circuit to short circuit) scanning (REV) under AM1.5G illumination, c) SPO from maximum power point tracking of tandem device under AM1.5G illumination, and d) IPCE of individual subcell in tandem device.

3. Conclusion

We have developed a novel thermionic emission-based ICL for monolithic all-perovskite tandem solar cells with solution-processed absorbers. A new FSIP hybrid system was introduced into the ICL of all-perovskite tandem solar cell for achieving the solvent resistance and defect passivation functions. The solvent resistance is to protect the bottom perovskite film from the penetration of polar solvents of upper perovskite solution. The defect passivation function is to reduce the defect concentration at perovskite surface and thus suppress the nonradiative recombination at the perovskite/ETL interface and significantly enhance the tandem solar cell performance. Besides the above functions, the ICL is indium-free and possesses good electrical conduction and high optical transmission especially in the infrared spectra. Fundamentally, thermionic emission plays an important role in the efficient carrier transport of ICL composed with the interlayers FSIP and BCP, which facilitates electron transport from sub-cell to the metal electrode and thus improves the tandem cell performance. Using the optimized ICL, the monolithic all-perovskite tandem solar cells demonstrate highest PCE up to 17.9% (from $J-V$ scan) with negligible hysteresis and the highest steady-state efficiency is 16.1% for a typical device. To our knowledge, they are the highest PCEs among monolithic all-perovskite tandem cells with solution-processed absorbers and indium-free ICL. This work contributes to monolithic all-perovskite tandem solar cells for emerging high-efficiency photovoltaics.

4. Experimental Section

Device Modeling Method: A drift–diffusion model is adopted to study carrier transport properties of the ICL. The detailed information of the model and the parameters used are listed in the Supporting Information.

Solar Cell Fabrication, Measurement, and Characterization: The materials, fabrication, measurements, and characterization methods are described in the Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

defect passivation, indium-free interconnecting layer, monolithic all-perovskite tandem solar cells, solvent resistance, thermionic emission

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