Precursor Engineering of the Electron Transport Layer for Application in High-Performance Perovskite Solar Cells

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The electron transport layer (ETL) is a key component of regular perovskite solar cells to promote the overall charge extraction efficiency and tune the crystallinity of the perovskite layer for better device performance. The authors present a novel protocol of ETL engineering by incorporating a composition of the perovskite precursor, methylammonium chloride (MACl), or formamidine chloride (FACl), into SnO$_2$ layers, which are then converted into the crystal nuclei of perovskites by reaction with PbI$_2$. The SnO$_2$-embedded nuclei remarkably improve the morphology and crystallinity of the optically active perovskite layers. The improved ETL-to-perovskite electrical contact and dense packing of large-grained perovskites enhance the carrier mobility and suppress charge recombination. The power conversion efficiency increases from 20.12% (blank device) to 21.87% (21.72%) for devices with MACl (FACl) as an ETL dopant. Moreover, all the precursor-engineered cells exhibit a record-high fill factor (82%).

1. Introduction

Perovskite solar cells (PSCs) have been developed as a novel type of solar cell with significant potential in the field of advanced photovoltaic technology.$^{[1–3]}$ Their power conversion efficiency (PCE) has rapidly improved over the past decade, increasing from 3.8% at their inception to over 25% at present.$^{[4–7]}$ The electron transport layer (ETL) in PSCs plays an indispensable role in transporting electrons, while simultaneously blocking holes. In a regular n-i-p type PSC of planar configuration, the structure of the ETL has a significant effect on the morphology and crystallinity of its neighboring perovskite layers.$^{[8–19]}$ Therefore, considerable research has been devoted to improving the PSC performance via ETL modification.$^{[20–31]}$ SnO$_2$ nanocrystals are a widely used ETL material that can be oriented so as to facilitate the vertical growth of the perovskite crystals, a morphology essential to charge carrier transport. In addition, a suitable structural modification of the SnO$_2$ ETL can result in an enhanced ETL-perovskite interfacial contact as well as increased pack densification and grain size of the perovskite crystals, which, in turn, increase the fill factor (FF) and stability of the PSC devices.$^{[32,33]}$

The additive engineering of perovskite precursors has been performed extensively to increase the crystallinity of optically active perovskite layers and hence, improve the device performance.$^{[34–40]}$ In this regard, Kim et al. investigated the addition of a methylammonium chloride (MACl) precursor to a formamidinium lead iodide (FAPbI$_3$) perovskite, and reported a significant improvement in the quality of the resultant perovskite films in terms of an increased grain size, crystallinity, and photoluminescence lifetime.$^{[34]}$ Zhou et al. proposed a perovskite formation mechanism using a formamidine chloride (FACl) dopant, which effectively increased the size and crystallinity of the perovskite crystallites.$^{[35]}$ Although perovskite precursors have proven effective in optimizing the performance of optically active layers, their application in SnO$_2$ ETLs has been rarely reported in the literature.$^{[41]}$

Herein, we report a facile and effective process for ETL modification through the addition of a perovskite precursor. Initially, two predetermined precursor compositions, specifically MACl and FACl, were introduced into the SnO$_2$ layers. These dopants facilitated the nucleation of perovskite nuclei embedded within the ETLs, leading to an improvement in the quality of the perovskite layers while also increasing the SnO$_2$-perovskite contact. In comparison to the PCE exhibited by the undoped device (20.12%), the MACl- and FACl-doped devices exhibited improved PCEs of 21.87% and 21.72%, respectively. The improvement in the photovoltaic performance of these PSCs was attributed to the perovskite precursor engineering of the ETLs, which imparted enhanced perovskite film morphology, reduced free charge carrier trap density, and increased FF. This study practically demonstrates the effectiveness of the perovskite precursor engineering of the ETL to significantly improve the performance of PSCs.

2. Results and Discussion

Figure 1a shows a schematic detailing the process of embedding perovskite crystal nuclei into the ETL. First, the mixed SnO$_2$-
MACI/SnO2-FACl solution was spin-coated onto the fluorine-doped tin oxide (FTO) substrate surface and annealed. Scanning electron microscopy (SEM) images obtained from the SnO2-MACl and SnO2-FACl films are shown in Figure S1, Supporting Information. The ETLs doped with either MACI or FACI exhibited increased densification surface morphology, which promoted the development of perovskite grains.[42] Subsequently, the sample surfaces were coated with PbI2 and annealed at 70 °C. During annealing, PbI2 reacts with the MACI or FACI present in the ETL to form perovskite crystal nuclei. As shown in Figure S2, Supporting Information, the samples doped with MACI or FACI (Figure S2a,b, Supporting Information) exhibited a significantly larger grain size than the undoped samples (Figure S2c, Supporting Information), suggesting the formation of perovskite grains in the doped samples. The X-ray diffraction (XRD) spectrum (Figure S3, Supporting Information) exhibits a peak at 31.89°, which corresponds to that of a perovskite crystal, confirming its formation.[43–45] A schematic of the SnO2-MACI/FACI ETL device is shown in Figure 1b. The perovskite crystal nucleus was embedded in the SnO2 ETL, which promoted the formation and development of perovskite particles.

The effect of MACI/FACI on the surface energy of the SnO2 ETLs was evaluated using ultraviolet photoelectron spectroscopy (UPS) and ultraviolet-visible spectroscopy (UV–Vis). The Fermi level (EF), valence band (EV), and conduction band (EC) were obtained directly from the recorded UPS and UV–Vis spectra (Figure S4, Supporting Information). In accordance with the energies shown in Table S1, Supporting Information, the energy-level diagram of each device is plotted in Figure 1c. The spectra generated by each of the three ETLs exhibited significant variations. In comparison with the pure SnO2 ETL, the EC values exhibited by the SnO2-MACI/FACI ETLs were close to that of a perovskite film, a property which is beneficial during the extraction and transfer of photogenerated electrons from the perovskite film to the SnO2-MACI/FACI ETLs.

To study the effect of a MACI/FACI-doped ETL on the crystallinity of perovskite films, the perovskite films derived from the SnO2-MACI, SnO2-FACI, and pure SnO2 ETL substrates were analyzed using XRD. As shown in Figure 1d and Figure S5, Supporting Information, the diffraction peaks corresponding to the (110) and (220) planes of the perovskite films are significantly stronger and sharper in the spectra of the SnO2-MACI/FACI-containing ETL samples in comparison to those of the pure SnO2 ETL sample, and the full width at half maximum values of the (110) peak are reduced (Table S2, Supporting Information). This result suggests that the crystallinity of the perovskite films was significantly enhanced upon doping with MACI/FACI.[46] The above results were consistent with the SEM characterization results shown in Figure 2.

The morphologies of the perovskite films obtained using the SnO2-MACI, SnO2-FACI, and pure SnO2 ETL substrates were evaluated using SEM. In comparison with the perovskite films containing a pure SnO2 ETL (Figure 2c), the perovskite films containing SnO2-MACI/FACI ETLs (Figure 2a,b) exhibited a significantly larger grain size, with a maximum value of 5 μm. An increase in the grain size will lead to a decrease in the grain boundary concentration, thereby reducing the capacity for carrier recombination at grain boundaries and nonradiative recombination loss.[47] According to the nucleation theory, the growth of the perovskite film consists of four processes: the first step is to generate the crystal nuclei; the second step is to grow into an island structure; the third step further evolves into the network structure; and the last step is to form a continuous layer.[13] In the samples modified by MACI and FACI, perovskite nuclei have been formed in the process of spin coating PbI2 and annealing. Therefore, it can directly evolve into island structure on the basis of existing nuclei, form a networked microstructure, and grow into continuous films. Figure 2d–f shows cross-sectional SEM images obtained from the three PSCs containing pure SnO2, SnO2-MACI, and SnO2-FACI ETLs. The perovskite particles that
developed on the pure SnO$_2$ ETL exhibited a random distribution with respect to their orientation (Figure 2f). However, the single grains developed on the perovskite films obtained using SnO$_2$-MACl/FACl ETLs were oriented vertically with respect to both, the ETL and hole transport layer (HTL) (Figure 2d,e), a configuration which is conducive to charge transmission in PSCs.$^{[32,33]}$

The extent of the interaction between SnO$_2$ and the MACl/FACl dopants was evaluated using infrared (IR) spectroscopy and X-ray photoelectron spectroscopy (XPS). In the IR spectra shown in Figure 3a, a peak occurs at 1640 cm$^{-1}$ in both, the SnO$_2$-MACl and SnO$_2$-FACl samples. This peak corresponds to the vibration of the N–H bond, which is related to the presence of MA$^+$/FA$^+$ ions.$^{[48]}$ However, comparing the IR spectra of FACl and SnO$_2$-FACl, it was found that the characteristic transmission band of C≡N originally appeared at 1720 cm$^{-1}$ in FACl samples disappeared in SnO$_2$-FACl samples, indicating that FA$^+$ ions bind to hydroxyl groups on SnO$_2$ surface through C≡N bonds.$^{[41,48]}$ XPS curve of O1s level in Figure S6, Supporting Information, also proves the above phenomenon. The XPS spectrum of O1s of all samples can be deconvoluted into two different peaks, corresponding to the hydroxyl group (OH$^-$) on the surface of SnO$_2$ (532.2 eV) and the saturated oxygen (O$_{2^-}$) in SnO$_2$ (530.3 eV)$^{[12]}$. It can be seen that the ratio of OH$^-$ peak to O$_{2^-}$ peak of SnO$_2$-MACl sample is only slightly lower than that of pure SnO$_2$ sample, while the ratio of SnO$_2$-FACl samples decreased significantly$^{[12]}$ which are consistent with the results of SEM image of Figure S1, Supporting Information. The survey XPS profiles in Figure 3b confirm the presence of N, Cl, Sn, and O in the SnO$_2$-MACl/FACl samples.$^{[49,50]}$ Figure 3c compares the Cl 2p XPS profiles of the SnO$_2$-MACl, SnO$_2$-FACl, and pure SnO$_2$ samples. The results suggest that SnO$_2$ was successfully modified through the addition of MACl/FACl. The Sn 3d XPS profiles in Figure 3d show that the Sn 3d double peaks arising from the SnO$_2$-MACl and SnO$_2$-FACl samples undergo a shift to a higher photoelectron binding energy in comparison to the pure SnO$_2$ sample, suggesting that the introduction of Cl in the sample induced a negative charge in the vicinity of the Sn atom.$^{[42,50]}$ Figure S7, Supporting Information, shows the UV–Vis absorption spectra of perovskite films deposited on SnO$_2$-MACl, SnO$_2$-FACl, and pure SnO$_2$ ETLs. It can be seen that the addition of MACl and FACl will not affect the absorption edge and absorption intensity of perovskite films.

To study the effect of the MACl and FACl dopants on electron transfer in the PSCs, the current density–voltage ($J$–$V$) trend exhibited by each sample was evaluated. Figure 4a–c shows the optimal $J$–$V$ performance exhibited by each of the three devices. The SnO$_2$-MACl- and SnO$_2$-FACl-based PSCs exhibited reverse-scan PCEs of up to 21.87% and 21.72%, respectively, significantly higher than the PCE of the pure SnO$_2$ PSC (20.12%). This was primarily attributed to a significant increase in both, the FF from 0.764 to 0.818 and 0.819, and the open-circuit voltage ($V_{OC}$) from 1.147 to 1.152 and 1.149 V in the SnO$_2$-MACl- and SnO$_2$-FACl-based PSCs, respectively. In addition, the short-circuit current density ($J_{SC}$) increased from 22.96 to 23.21 and 23.08 mA cm$^{-2}$ in the SnO$_2$-MACl- and SnO$_2$-FACl-based PSCs, respectively. Further, the SnO$_2$-MACl and SnO$_2$-FACl-based ETLs essentially eliminate any hysteresis, suggesting that both, the SnO$_2$-MACl and SnO$_2$-FACl ETLs, exhibit stronger charge transfer capabilities than the pure SnO$_2$ ETL. Figure 4d shows the external quantum efficiency (EQE) spectra of the SnO$_2$-MACl, SnO$_2$-FACl, and pure SnO$_2$ ETL PSCs. Analysis of these spectra revealed that the integrated current densities of the three PSCs were 22.87, 22.79, and 22.74 mA cm$^{-2}$, respectively, values which were consistent with the $J$–$V$ measurement results. Concurrently, the stabilized photocurrent output of PSCs with the SnO$_2$-MACl, SnO$_2$-FACl, and single SnO$_2$ ETLs were recorded at the maximum power...
Steady-state PCEs of 20.8%, 20.3%, and 18.9% were respectively obtained.

Figure 5a–d shows the statistical distribution of the $V_{OC}$, $J_{SC}$, FF, and PCE values of each of the PSC samples. The average $V_{OC}$ values exhibited by the PSCs based on SnO$_2$-MACl and SnO$_2$-FACl ETLs were 1.141 and 1.140 V, respectively, which were higher than those exhibited by PSCs based on a pure SnO$_2$ ETL (1.130 V). In addition, the average $J_{SC}$ values exhibited by the PSCs based on SnO$_2$-MACl and SnO$_2$-FACl ETLs were 22.59 and 22.39 mA cm$^{-2}$, respectively, which were higher than those exhibited by PSCs based on a pure SnO$_2$ ETL (22.13 mA cm$^{-2}$). The average FFs exhibited by the PSCs based on SnO$_2$-MACl and SnO$_2$-FACl ETLs were 0.786 and 0.785, respectively, which were significantly higher than those exhibited by PSCs based on a single SnO$_2$ ETL (0.730). Overall, the average PCEs of the PSCs based on SnO$_2$-MACl and SnO$_2$-FACl ETLs were 20.27% and 20.08%, respectively, which were significantly higher than those of the PSCs based on single SnO$_2$ ETLs (18.37%). The improvement in the photovoltaic properties exhibited by the doped PSCs was attributed to the improvement in the surface morphology of the perovskite films. These improvements facilitated a reduction in the trap density, which imparted an increased FF in the corresponding PSCs.

Steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) were used to evaluate the charge dynamics between the perovskite and ETL. In comparison to the pure SnO$_2$ ETL, the PL intensities exhibited by the perovskite films deposited on the SnO$_2$-MACl/FACl-based ETLs were significantly reduced (Figure 6a). This result suggests that SnO$_2$-MACl/FACl-based ETLs enhance electron extraction and transport at the interface. This result was further validated by the TRPL results shown in Figure 6b. The PL decay of the perovskite films deposited on SnO$_2$-MACl/FACl-based ETLs occurred at an increased rate in comparison to the perovskite films deposited on pure SnO$_2$ ETLs. The corresponding lifetimes of the perovskite films deposited on the SnO$_2$-MACl, SnO$_2$-FACl, and single SnO$_2$ ETLs were 150, 184, and 273 ns, respectively.

The charge transfer mechanisms of the PSCs were investigated further via electrochemical impedance spectroscopy (EIS). The resultant Nyquist plots (Figure 6c) were obtained by placing the PSCs in dark conditions under a 5 V bias, while the contact resistance ($R_{co}$) and recombination resistance ($R_{rec}$) were obtained by fitting the recorded results (Table S3, Supporting Information). The reduced $R_{co}$ values exhibited by PSCs utilizing SnO$_2$-MACl/FACl-based ETLs suggest that SnO$_2$-MACl/FACl enhanced the charge transfer ability of the cells in comparison to the pure SnO$_2$ samples.$^{[42,50]}$

To investigate the stability of the PSC devices, a sample of each composition was stored in a glove box to simulate the aging process. Figure 6d shows the resultant PCEs of all three PSCs. Although the PSCs stored in the glove box were not susceptible to corrosion by oxygen and water, they were still affected by interface diffusion, ion migration, and electrode corrosion. After an aging period of 500 h, the PSCs based on the SnO$_2$-MACl/FACl ETLs...
Figure 4. Optimal J–V curves of the typical PSCs obtained using the a) SnO₂-MACl, b) SnO₂-FACl, and c) pure SnO₂ ETLs. d) EQE spectra of the typical PSCs obtained using the SnO₂-MACl, SnO₂-FACl, and pure SnO₂ ETLs.

exhibited efficiencies of 90% with respect to their original values, while those based on a pure SnO₂ ETL exhibited efficiencies of just 70% with respect to their original values. These results suggest that the stability of PSCs based on SnO₂-MACl/FACl ETLs is significantly higher than that of their pure SnO₂ ETL counterparts.

3. Conclusion

In summary, a novel process for the modification of ETLs using perovskite precursors was proposed. MACl/FACl perovskite precursors were integrated into the ETL microstructures to form the perovskite nuclei. The perovskite crystal nuclei embedded within the ETL microstructures promoted the development of perovskite crystals, leading to the formation of perovskite films with larger grains and increased crystallinity. The thus-formed dense and pore-free films suppressed defect formation and improved the FF of the device, thereby improving the PCE of the corresponding PSC. The introduction of MACl or FACl into the ETLs significantly improved the FF of the PSCs, and from 0.764 to 0.818 and 0.819, respectively. The overall PCEs of the two PSCs doped with MACl and FACl were 21.87% and 21.72%, respectively. The PCEs recorded for both the doped PSCs were significantly higher than those recorded for the unmodified device (20.12%). The results of this study should provide a strong basis for the preparation of a PSC with enhanced performance and large perovskite grains, through the modification of the ETL.

4. Experimental Section

Materials: FTO was purchased from OPVtech (China). Tin (IV) oxide (SnO₂) nanoparticles (15% in H₂O, colloidal dispersion) were purchased from Alfa Aesar. Lead (II) iodide (PbI₂) (99.99%, trace metals basis), for use in the perovskite precursor, was obtained from Tokyo Chemical Industry Co., Ltd. Methylammonium chloride (CH₃NH₃Cl) (MACl) (99.5%, subjected to four rounds of purification), formamidinium chloride (HC(NH₂)₂Cl) (FACl) (99.5%, subjected to four rounds of purification), methylammonium bromide (CH₃NH₃Br) (MABr) (99.5%, subjected to four rounds of purification), formamidinium iodide (HC(NH₂)₂I) (FAI) (99.5%, subjected to four rounds of purification) were purchased from Xi’an Polymer Light Technology Corp. 2,2′,7,7′-tetrakis-(N,N-di-p-methoxyphenylamine)-9,9′-spirobifluorene (Spiro-OMeTAD) (99.86%) was purchased from Advanced Electron Technology. N,N-dimethylformamide (DMF) (99.8%), dimethyl sulfoxide (DMSO) (99.9%), chlorobenzene
Figure 5. Statistical distributions of the a) $V_{OC}$, b) $J_{SC}$, c) FF, and d) PCE values of typical PSCs based on the SnO$_2$-MACl, SnO$_2$-FACl, and pure SnO$_2$ ETLs (data collected from 30 cells).

Figure 6. a) Steady-state photoluminescence (PL) and b) time-resolved photoluminescence (TRPL) spectra exhibited by perovskite films deposited on the SnO$_2$-MACl, SnO$_2$-FACl, and pure SnO$_2$ ETLs. c) Nyquist plots obtained under dark conditions from the PSCs derived from the SnO$_2$-MACl, SnO$_2$-FACl, and pure SnO$_2$ ETLs. d) Long-term stability performance exhibited by the PSCs derived from the SnO$_2$-MACl, SnO$_2$-FACl, and pure SnO$_2$ ETLs without encapsulation under ambient conditions.
was dissolved in 1 mL of CB. Subsequently, 73 mg of Spiro-OMeTAD, MACl, SnO2-FACl, and pure SnO2 films were measured and recorded.

Device Fabrication: The FTO glass was sequentially cleaned using deionised water, acetone, and isopropanol in an ultrasonic bath before being dried. Prior to use, the FTO glass was treated with oxygen plasma for 1 min. Subsequently, 0.2 mL of both MACl or FACl were then added to the solution. Once a uniformly dispersed solution was obtained via stirring, the solution was spin-coated onto the FTO surface at 4000 rpm for 30 s, and then the MACl modified substrate and FACl modified substrate were annealed for 30 min at 120 and 400 °C, respectively, to produce the ETL. Subsequently, 1.5 mL of PbI2 was dissolved in a DMF-DMSO (9:1 volume ratio) mixed solvent and stirred overnight. The homogeneous solution was then spin-coated onto the surface of the ETL at 1500 rpm for 30 s, prior to annealing at 70 °C for 1 min. Meanwhile, an FAI:MABr:MACl (270:27:27 mg in 3 mL IPA) mixed solution was prepared and spin-coated onto the PbI2 surface at 2000 rpm for 30 s, prior to annealing at 150 °C for 15 min in ambient air (≈40% humidity) to form the perovskite layer. Subsequently, 73 mg of Spiro-OMeTAD was dissolved in 1 mL of CB. Following this, 16.8 μL of LiTFSI (520 mg mL⁻¹ in acetonitrile), 27.6 μL of cobalt (II) FK209 (300 mg mL⁻¹ in acetonitrile), and 27.6 μL of 4-tert-butylpyridine were added to the solution to prepare the final HTL precursor solution. The HTL precursor solution was then spin-coated onto the perovskite film at 3000 rpm for 30 s. Finally, an 80 nm Au film was deposited on the outer layer of the device through thermal evaporation.

Characterisation: Scanning electron microscopy (SEM) (Hitachi, SU8010) was used to evaluate the microstructure of the ETLs and perovskite films. The crystal structure and mass of the PbI2 and perovskite films were characterized by X-ray diffraction (Shimadzu XRD-7000). UPS of the SnO2-MACl, SnO2-FACl, and single SnO2 films was performed using a He I (21.22 eV) excitation line (Thermo Scientific ESCAlab 250Xi). UV–Vis absorption spectra of the SnO2-MACl, SnO2-FACl, and pure SnO2 films were obtained (Agilent Cary60). The MACl, FACl, SnO2-MACl, and SnO2-FACl samples were subjected to Fourier transform infrared (FTIR) analysis (IRPrestige-21). The photoluminescence (PL) of the perovskite films deposited on the SnO2-MACl, SnO2-FACl, and pure SnO2 films was measured and recorded (Hitachi F-4600, 470 nm excitation). Electrochemical impedance spectroscopy (EIS) was performed on the PSSCs based on the SnO2-MACl, SnO2-FACl, and pure SnO2 ETLs, using a scanning frequency between 1 and 10⁶ Hz, and an AC amplitude of 5 mV (ZAHNER PP211). The external quantum efficiencies (EQEs) of the PSSCs based on the SnO2-MACl, SnO2-FACl, and single SnO2 ETLs were obtained in the wavelength range of 330–870 nm (EnliTech QE-R). The current density–voltage (J–V) characteristics of the PSSCs derived from the SnO2-MACl, SnO2-FACl, and pure SnO2 ETLs were measured in air without encapsulation under AM 1.5G illumination (Keithley 2400 Source Meter), for which each of the PSSCs were covered with a metal aperture mask to define a active area of 0.1 cm².

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.

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Research Data are not shared.

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