Employing 2D-Perovskite as an Electron Blocking Layer in Highly Efficient (18.5%) Perovskite Solar Cells with Printable Low Temperature Carbon Electrode

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Interface engineering and passivating contacts are key enablers to reach the highest efficiencies in photovoltaic devices. While printed carbon-graphite back electrodes for hole-transporting material (HTM)-free perovskite solar cells (PSCs) are appealing for fast commercialization of PSCs due to low processing costs and extraordinary stability, this device architecture so far suffers from severe performance losses at the back electrode interface. Herein, a 2D perovskite passivation layer as an electron blocking layer (EBL) at this interface to substantially reduce interfacial recombination losses is introduced. The formation of the 2D perovskite EBL is confirmed through X-ray diffraction, photoemission spectroscopy, and an advanced spectrally resolved photoluminescence microscopy mapping technique. Reduced losses that lead to an enhanced fill factor and \( V_{\text{OC}} \) are quantified by electrochemical impedance spectroscopy and \( J_{\text{SC}} - V_{\text{OC}} \) measurements. This enables reaching one of the highest reported efficiencies of 18.5% for HTM-free PSCs using 2D perovskite as an EBL with a significantly improved device stability.

1. Introduction

The device architecture of perovskite solar cells (PSCs) has evolved tremendously over the years yielding to what is known nowadays as state-of-the-art PSCs for n-i-p configurated devices.[1–4] This consists of a transparent conductive oxide (TCO) as a front contact electrode on which electron transport layers (ETLs), a perovskite light absorber, and an organic hole-transporting material (HTM), namely 2,2',7,7'-tetrakis-(N,N-di-p-methoxy-phenyl-amine)-9,9'-spirobifluorene (spiro-OMeTAD), are sequentially deposited followed by a metal contact electrode, usually gold (Au). Such devices have been reported to yield the highest efficiencies, currently, 25.8% (25.5% certified), approaching those achieved through established silicon photovoltaic devices.[5–7] This demonstrated rapid growth in efficiency has brought considerable attention toward pushing the up-scalability and commercialization of PSCs given their ease of manufacturing processes and low material costs. However, despite the high achieved power conversion efficiency (PCE), the stability of PSCs still needs to be improved to meet the market requirements. For instance, metal contact electrodes can stimulate degradation of PSCs due to diffusion of metal impurities across the interfaces.[8–11] This problem can be fundamentally overcome by replacing the metal contact with chemically inert materials.

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and robust carbon–graphite electrodes in PSCs (C-PSCs), which are highly promising for commercialization due to their ambient pressure processability based on industrially established printing techniques. However, the use of an organic HTM in C-PSCs remains challenging. The solvents of the so far investigated low-temperature curable carbon pastes are incompatible with highly efficient organic HTMs, while the solvents in high-temperature curable graphite-based pastes require sintering temperatures over 400 °C, which makes it impossible to incorporate organic HTMs. Thus, the direct contact of the perovskite absorber and the carbon electrode can be problematic considering that one of the dominant loss mechanisms in the HTM-free C-PSCs was found to be surface recombination at the perovskite/carbon interface.

Surface passivation of solution-processed perovskite light absorbers can be a strategy to mitigate the loss mechanism at the interface. One of the most widely adopted approaches is to introduce a low-dimensional (2D or quasi-2D) perovskite layer on top of the 3D perovskite photo-absorber. The surface passivation can effectively suppress undesirable non-radiative recombination by reducing the density of defects at the 3D perovskite/carbon electrode interface. Moreover, the energetic barrier induced by the higher conduction band of the 2D perovskite passivation layer compared to the 3D perovskite can effectively block electron back transfer. Furthermore, the use of 2D perovskites having bulky ammonium cations can improve the stability of PSCs by protecting the underlying layers from external degradation factors such as moisture diffusion.

In this work, we employed a 2D perovskite as an electron blocking layer (EBL) with its implementation of surface passivation on top of a 3D perovskite layer in HTM-free C-PSCs. The formation of the 2D perovskite EBL was achieved by the deposition of octylammonium iodide (OAI) on top of the 3D perovskite FAPbI₃ to effectively block electron back transfer. Furthermore, the use of 2D perovskites having bulky ammonium cations can improve the stability of PSCs by protecting the underlying layers from external degradation factors such as moisture diffusion.

2. Results and Discussion

2.1. Device Concept and Formation of 2D Perovskite on 3D Perovskite

The device stack of the C-PSC in question for this study consists of an FTO coated glass substrate, a compact titanium dioxide (c-TiO₂) hole blocking layer, a mesoporous titanium dioxide (m-TiO₂) electron selective layer, and a solution-processed 3D perovskite FAPbI₃ photo-absorber layer. We deposited octylammonium iodide (OAI) on top of the 3D perovskite FAPbI₃ to form the 2D perovskite EBL. The carbon paste was blade coated last and cured at low temperature (<120 °C), which resulted in a ≈28 µm thick back electrode layer (Figure 1 and Figure S1, Supporting Information).

Perovskite thin films on glass with and without 2D perovskite were analysed to confirm its formation. While both films exhibited absorbance of FAPbI₃ with an onset at ≈810 nm (Figure 2a), the 3D/2D perovskite film resulted in an additional absorption onset at 583 nm, which can be attributed to resolved photoluminescence (PL) measurements. The employment of the 2D perovskite EBL effectively suppressed non-radiative recombination thanks to its asymmetric band offset from the adjacent 3D perovskite, blocking undesirable electron back transfer. Comparative JSC–VOC measurements and electrochemical impedance spectroscopy (EIS) gave insights into the reduced interfacial transport losses. We demonstrated that the HTM-free C-PSCs employing a 2D perovskite EBL resulted in a PCE of 18.5%, which is to the best of our knowledge among the highest reported in the corresponding device architecture using low-temperature processed carbon electrodes, while the otherwise identical device without the 2D perovskite EBL showed inferior PCE of 15.7%. Furthermore, the device with the 2D perovskite EBL showed a great improvement in terms of long-term stability maintaining a PCE of over 82% of its initial efficiency after 500 h of continuous 1-sun illumination while the device without the EBL had dropped to ≈63% of its initial efficiency after only 200 h.

Figure 1. a) Schematic diagram of the investigated low-temperature carbon electrode-based PSC with 3D/2D perovskite treated by OAI. b) Scanning electron microscopy (SEM) image overlapped with the energy-dispersive X-ray spectroscopy (EDX) map of the cross-section of HTM-free low-temperature carbon-electrode perovskite devices.
the formation of the 2D passivation layer. To corroborate its formation, we performed X-ray diffraction (XRD) measurements of the 3D perovskite and the layer-by-layer deposited 3D/2D perovskite films. Both films showed a typical diffraction pattern of 3D FAPbI$_3$ having main peaks at 14.2° and 28.3° originating from (100) and (200) planes, respectively (Figure 2b), but the diffraction of 3D perovskite without 2D perovskite had an additional peak at 12.9° which can be attributed to the use of excess PbI$_2$ (Figure 2c). In contrast, the deposition of OAI resulted in the removal of PbI$_2$ diffraction peak due to its chemical interaction with OAI and the formation of 2D perovskite that gave rise to new diffraction peaks at 3.9°, 7.5°, and 11.2° indexed to the planes (002), (004), and (006), respectively, corresponding to (OA)$_2$PbI$_4$.[19,20]

X-ray photoelectron spectroscopy (XPS) also manifested the formation of 2D perovskite (Figure 2d). In the C 1s spectrum of the 3D perovskite, two dominant peaks were detected at 285.3 and 288.6 eV. The signal with lower energy can be ascribed to the integration of C–H or C–C of FA, and the other signal can be assigned to the formation of C$\equiv$O bonds by the decomposition and oxidation of 3D perovskite.[21] Upon the deposition of OAI on top of the 3D perovskite, the peak intensity at the lower energy significantly increased due to the formation of 2D perovskite including a larger number of C$\equiv$H and C$\equiv$C bonds. Also, a signal at 286.6 eV became discernable, which can be explained by the increased number of C–N bonds in the 2D perovskite.[15] Meanwhile, we observed a decrease in the intensity of C$\equiv$O bonds in the 3D/2D perovskite film, implying that the decomposition and oxidation of the underlying 3D perovskite by oxygen and moisture were mitigated due to the 2D perovskite at the surface.[22] In the N 1s spectra, the peak at 400.8 eV in both films can be assigned to –NH$_2$ of FA, but the additional peak at 402.6 eV in the 3D/2D perovskite film can originate from –NH$_3^+$ of octylammonium in the 2D perovskite.[23] In the O 1s spectra, interestingly, the sole peak of the 3D perovskite was completely removed by the formation of the 2D perovskite that effectively suppressed the oxidation of the film owing to its high thermodynamic stability.[24] In the Pb 4f spectra, the 3D perovskite film exhibited main signals of Pb of FAPbI$_3$ at 138.6 and 143.5 eV. Also, we observed weak signals at lower binding energies (136.8 and 141.4 eV) which can be attributed to metallic Pb at the surface of the 3D perovskite.[25] On the other hand, the 3D/2D perovskite film, having the main signals at 138.6 and 143.5 eV, showed stronger signals of Pb at the lower binding energies at 136.8 and 141.4 eV. We surmise that the intensity increase of the signals can be ascribed to Pb element of the 2D perovskite.[26,27] To be specific, the stronger bonding between organic ammonium and iodide of 2D perovskite than that of 3D perovskite can induce relatively less binding of the Pb element of the PbI$_6$, which may result in the strengthening of the signals at the low binding energies.

2.2. Energy Level Alignment between 3D and 2D Perovskites and Its Effect on Electron Blocking

We conducted ultraviolet photoemission spectroscopy (UPS) to investigate the energy levels of the perovskite films (Figure 3a). Both onset and secondary cut-off energy values were determined based on the logarithmic scale, which resulted in the ionization potential (IP) energy of the 3D and 2D perovskite films as 5.40 and 5.43 eV, respectively. In order to determine the electron affinity of the 3D and 2D perovskites, we calculated the optical bandgap energy ($E_g$) of each perovskite by
Tauc plot (Figure 3b). Both films yielded an $E_g$ of 1.55 eV of the 3D perovskite. This implies that the underlying 3D perovskite remained intact upon the formation of the 2D perovskite on its surface. On the other hand, in the higher energy region, the 3D/2D perovskite film revealed an additional increase in the line due to the absorption by the 2D perovskite yielding to an $E_g$ of 2.13 eV, whereas the 3D perovskite film resulted in an almost linear line which indicates the absence of the 2D perovskite. Based on the IP energy and $E_g$ of the perovskites, we present the energy band diagrams of both systems with and without the 2D perovskite EBL (Figure 3c). In the system without the 2D perovskite EBL, the problematic electron back transfer to the carbon electrode can easily occur resulting in non-radiative recombination at the perovskite/carbon interface. By employing the 2D perovskite EBL, in contrast, due to the asymmetric band offset mainly of conduction band energy of 0.55 eV, effective blocking of the undesirable electron back transfer to the carbon electrode can be facilitated, leading to the suppression of non-radiative recombination, and high hole selectivity at the interface.\cite{28} Additionally, we plotted the UPS spectra based on the linear scale of the photoemission intensity (Figure S2, Supporting Information), which resulted in a similar trend of energy levels of the perovskites despite different absolute energy values. We summarized the energy values obtained either by the logarithmic or linear plots in Table S1 (Supporting Information).

Figure 3. a) UPS spectra of 3D and 3D/2D perovskites showing secondary cut-off (left) and onset (right) on the logarithmic scale of photoemission intensity. b) Tauc plot of 3D and 3D/2D perovskites. c) Schematic energy band diagram of 3D perovskite without 2D perovskite EBL (left) and with 2D perovskite EBL (right).

Figure 4. a) Photoluminescence spectra of 3D and 3D/2D perovskite films on glass probed from the perovskite side, b) µPL maps of 3D/2D perovskite film, which was imaged from the perovskite side, displaying the normalized PL intensity maps of the 2D (top) and the 3D (bottom) perovskite layer.
2.3. Microscopic Imaging of 2D Perovskite Electron Blocking Layer

To ensure the effective blocking of electron back transfer to the carbon electrode, a homogeneous 2D perovskite layer with full coverage throughout the entire active area is essential. To assess the quality of the 2D perovskite film coverage and homogeneity of phase purity, we employed a novel microscopically resolved photoluminescence ($\mu$PL) mapping technique which enables a distinctive differentiation between the 3D and 2D perovskites. Therefore, a UV laser beam (355 nm) was focused on a confocal microscope setup onto the sample, which was scanned pixel by pixel with a laser spot size of $\approx 3 \mu$m (FWHM). The emitted PL signal was spectrally resolved by coupling it via a dichroic mirror to a Czerny–Turner type spectrometer and detecting the signal afterward with a silicon CCD camera.

Figure 4a shows the PL spectra for 3D and 3D/2D perovskite films on glass that were probed from the top side (i.e., illuminating the perovskite surface). The 3D film without the 2D perovskite EBL featured a PL peak at 813 nm of the 3D FAPbI$_3$ perovskite. In contrast, the 3D/2D perovskite film exhibited emission not only at 813 nm but also 514 and 567 nm which can be attributed to the emission of 2D perovskite with $n = 1$ and $n = 2$, respectively. As displayed in Figure 4b, by distinguishing the contribution of the two PL peaks, it is possible to map the PL intensities of the 2D perovskite layer (contribution between 555 and 595 nm, top image) and 3D perovskite layer (contribution between 780 and 820 nm, bottom image) individually. The PL signal of the 2D perovskite was present throughout the displayed area, which indicates complete coverage. In contrast, the PL map ascribed to the 3D perovskite displayed a higher inhomogeneity in the signal intensity. It is worthy of notice that the high PL regions of the 3D perovskite overlapped with the lower PL regions of the 2D perovskite. As the excitation light was partially absorbed by the 2D perovskite EBL, it is to be expected that, in regions where the 2D perovskite EBL was thinner, more excitation light was transmitted to the 3D perovskite and hence the PL signal assigned to this layer was higher. Finally, to assess the homogeneous layer deposition on a macroscopic scale, a full solar cell stack with and without 2D perovskite EBL was analyzed by a microscopically resolved laser beam-induced current (LBIC) mapping, which supports the finding of homogeneous coverage of the 2D perovskite on the 3D perovskite throughout the active area (Figure S3, Supporting Information). Moreover, the LBIC image indicates that the 2D capping layer may act as a protection layer against local damage induced by the blade coating of the carbon layer.

To evaluate the EBL characteristic of the 2D perovskite, we fabricated HTM-free C-PSCs using the 3D/2D perovskite and 2D PL imaging shown in Figure 5c,d can corroborate that the resulting phase was the 2D perovskite by the conversion of PbI$_2$ upon the deposition of OA1. The images display the same PL spectral ranges as stated above in Figure 4b. This $\mu$PL image exhibited sparsely distributed small granular patterns which correspond to the small grains observed in the SEM image. Meanwhile, the emission by 3D perovskite of the same film showed larger granular emitting patterns that can be attributed to the large-sized 3D perovskite grains.

2.4. Evaluation of 2D Perovskite Electron Blocking Layer in HTM-Free C-PSCs

To evaluate the EBL characteristic of the 2D perovskite, we fabricated HTM-free C-PSCs using the 3D/2D perovskite and
reference devices with only 3D perovskite for comparison. The champion C-PSC device incorporating the 2D perovskite EBL resulted in a PCE of 18.5%, a $V_{OC}$ of 1030.0 mV, a $J_{SC}$ of 24.3 mA cm$^{-2}$, and a FF of 73.9% while the otherwise-identical device without the 2D perovskite EBL had a PCE of 15.7%, a $V_{OC}$ of 1003.6 mV, a $J_{SC}$ of 24.1 mA cm$^{-2}$, and a FF of 64.5%. Figure 6a–d presents the statistics of the photovoltaic parameters of 10 devices for each configuration. With the use of 2D perovskite EBL, the average $V_{OC}$ was improved from 948 to 1013 mV, which can be attributed to reduced carrier recombination losses at the interface. This increase of 65 mV corresponds (at 300 K) roughly to a tenfold increase in the product of electron and hole concentrations at $V_{OC}$, assuming a diode ideality factor of 1.$^{[29,30]}$ In addition, the average FF was also increased from 57.5% to 68.1% possibly due to the reduction of carrier transport losses and a less optimal diode ideality factor. The forward and reverse $J$–$V$ curves of the champion HTM-free C-PSCs are shown in Figure S5 (Supporting Information). The hysteresis of the devices with and without 2D perovskite EBL was overall minor.

External quantum efficiency (EQE) measurements revealed a larger $J_{SC}$ mismatch for the device with 3D perovskite (Figure S6, Supporting Information). Although a current density mismatch between the $J_{SC}$ from $J$–$V$ measurements and the integrated $J_{SC}$ from EQE measurements has been commonly reported for PSCs due to the strong frequency dependency of the latter among other reasons.$^{[31,32]}$ We assign the more pronounced $J_{SC}$ mismatch recorded for the device without the 2D perovskite EBL to its degradation considering the long measurement time that EQE requires compared to $J$–$V$ measurements.

Figure 6e confirms the superior operation stability of the HTM-free PSCs with the use of 2D perovskite EBL. The devices were kept under continuous 1-sun illumination at maximum power point (MPP) in an inert atmosphere (N$_2$). For the C-PSCs without the EBL, a steeper decrease of device performance within the first 100 h was observed, followed by a stabilization and slight decrease to 60% of the initial efficiency after 500 h. With the use of 2D perovskite EBL, this initial performance loss was significantly reduced, and the device exhibited a more linear performance loss, still maintaining over 80% of the initial PCE at 500 h under MPP tracking. Also, the steady-state output of the devices was measured by tracking $V_{OC}$, $J_{SC}$, and PCE at fixed voltage under continuous 1 sun illumination. The use of the 2D perovskite EBL demonstrated improvement in the stability of the photovoltaic parameters with the less notable decrease over the 250 s (Figure S7, Supporting Information).

### 2.5. The Effect of 2D Perovskite EBL on Electrical and Photophysical Properties of C-PSCs

To understand the effect of the 2D perovskite EBL on the reduction of non-radiative recombination losses, we assessed the pseudo-FF (pFF) of the devices by steady-state $V_{OC}$ and $J_{SC}$ measurements at different light intensities (Figures S8 and S9, Supporting Information). The steady-state $V_{OC}$ measurement revealed a 62.5 mV voltage drop per decade of decreasing light intensity for the device with the 2D perovskite EBL while the device without the EBL exhibited a drop of 110.7 mV per decade of light intensity (Figure S8, Supporting Information). The steady-state $V_{OC}$ measurement.

It is noteworthy that an ideal Shockley diode is expected to exhibit a change of 60 mV per decade at 300 K.$^{[29,30]}$ This suggests that the corresponding diode ideality factor ($n_{id}$) of the...
device using the 2D perovskite EBL is close to the ideal value, namely $n_{id} = 1$, whereas the $n_{id}$ of the device without the EBL was found to be higher than 2 implying that non-radiative recombination is dominant and leads to a reduced FF value. Along with the result of the steady-state $J_{SC}$ at different light intensities (Figure S9, Supporting Information), we plotted the obtained $J_{SC} - V_{OC}$ pairs that yielded a pseudo-$J$–$V$ curve. As the effect of resistive losses can be neglected at open and short circuit, this pseudo-$J$–$V$ curve represents the $J$–$V$ characteristics of the device without the influence of charge transport losses. From these curves, the maximum achievable pseudo fill factor (pFF) of a device can be assessed by compensating for ohmic resistance losses.[33] Consequently, the pFF of the device with 2D perovskite EBL was found to be 86.3% which is greater than that of the device without the EBL (68.4%) (Figure 7a,b). The great difference between FF from the $J$–$V$ curve, and pFF from the pseudo-$J$–$V$ curve accounts for the contribution of charge transport losses to the photovoltaic performance of the device.

Also, the contribution of non-radiative losses to the FF can be assessed in the radiative limit (FF$_{rad}$), i.e., in the ideal case where the device performance is only limited by fundamental mechanisms such as transmission, thermalization, and radiative recombination in accordance with Shockley–Queisser approximation. Based on the energy bandgap of 1.55 eV of the 3D perovskite absorber employed here, the FF$_{rad}$ was calculated to be 90.3%. Consequently, non-radiative recombination contributed to a FF loss of 21.8% absolute for the device without the 2D perovskite EBL, while the device with the EBL showed only 3.95% absolute loss. This clearly proves that the 2D perovskite EBL effectively blocks electrons from interfacial non-radiative recombination.

To further investigate the reduced interfacial recombination losses by the introduction of the 2D perovskite EBL, electrochemical impedance spectroscopy (EIS) of PSCs was carried out.[36] The measurements were performed at a frequency range from 1 MHz to 100 mHz under an applied bias of $-0.6$ V. The Nyquist plot in Figure 7c showed two semicircles to which we fit the equivalent circuit model displayed in the inset. $R_s$ describes resistive losses at the “outside” of the cell, e.g., ohmic losses along the front and back electrode and the wirings. As the same device geometry was used, the $R_s$ was similar for both devices with 4.6 Ω cm$^2$ for the 3D/2D and 5.8 Ω cm$^2$ for the device using 3D perovskite.

Although the signals at the high (Left) and low (Right) frequency regimes have yet to be unambiguously interpreted in the literature considering the wide variety of EIS spectra reported for PSCs,[37] it is generally agreed that the semi-circle at the high frequency (HF) regime is associated with fast dynamics, i.e., electronic processes of photoexcited charge carriers such as charge transfer and trap-assisted non-radiative recombination. In contrast, the response at the low frequency...
(LF) regime should account for ion dynamics which can, in turn, impact the overall interfacial carrier dynamics.\cite{37-39} We obtained the resistance of 15.7 Ω cm² from the semi-circle at the HF regime ($R_{HF}$) of the device using the 2D perovskite EBL, which was lower than that without the 2D perovskite EBL (21.4 Ω cm²). Thus, considering that the 2D perovskite EBL is deposited at the 3D perovskite/carbon interface, the lower $R_{HF}$ suggests the reduction of the non-radiative recombination losses at the interface due to the role of the 2D perovskite in the blocking of the undesirable electron back transfer as well as trap passivation. On the other hand, the response at the LF regime which exhibited a more noticeable reduction with the use of the 2D perovskite EBL may be attributed to the mitigated ion accumulation at the hole interface. As the ion accumulation at the interface can lead to the formation of space charge which can facilitate non-radiative recombination at the hole interface, the reduced non-radiative recombination can be expected by employing the 2D perovskite EBL at the interface.

This interpretation is corroborated by simultaneous PL and $V_{OC}$ decay measurements. As further discussed in Figures S10 and S11 (Supporting Information), the 3D device revealed an overshoot of the $V_{OC}$ in combination with a rapid decay of the PL within the first few microseconds after the light is switched off. In a recent publication, we showed that such a decoupling between the PL intensity, i.e., quasi-Fermi-level (QFL) splitting or internal photovoltage ($iV_{QFL}$), and the externally measured $V_{OC}$ originates from a strong gradient of the majority charge carrier QFL in the vicinity of a nonideal contact.\cite{40} Supposedly this gradient occurs at the carbon contact due to an interplay between surface recombination current and conductivity limitation due to ionic space charge. The overshoot is suppressed by the introduction of a 2D perovskite EBL.

3. Conclusion

We report the development of low-temperature processed C-PSCs including a 2D perovskite electron blocking layer between the 3D perovskite absorber and the carbon back electrode. The use of a 2D perovskite EBL resulted in the effective suppression of interfacial non-radiative recombination and thus a higher photovoltage. We attributed the effects to the energy level alignment between the 3D and 2D perovskites at which undesirable electron back transfer to the carbon electrode can be blocked due to their difference in electron affinities (of the conduction band). We confirmed the formation of 2D perovskite EBL on top of the 3D perovskite by various characterization techniques. In particular, spectrally resolved PL microscopy mapping revealed a complete and homogeneous coverage of the 2D perovskite on the 3D perovskite, which contributed to the reduction of carrier loss by non-radiative recombination. Device characterization using EIS showed that the 2D perovskite EBL effectively reduced non-radiative recombination losses, thereby increasing FF.

Moreover, we quantified the contribution of the non-radiative recombination losses to the $V_{OC}$ and the FF through illumination-dependent $J_{SC}$-$V_{OC}$ measurements from which we found the mitigating effect of the 2D perovskite EBL on the reduction of non-radiative losses. The champion device using 2D perovskite EBL achieved a PCE of 18.5% which is, to the best of our knowledge, among the highest for HTM-free low-temperature processed C-PSCs. The employment of 2D perovskite EBL also improved the device long-term stability maintaining 82% of its initial efficiency after 500 h of constant 1-sun illumination. We believe that the approach of the employment of 2D perovskite as an EBL can help pave the way for the future practical development of fully printable C-PSCs with high efficiency and long-term stability.

4. Experimental Section

Materials: Formamidinium iodide (FAI), lead iodide (PbI₂), methylammonium chloride (MACI), octylammonium iodide (OAI), 4-tert-butylpyridine (tBP), and spiro-OMeTAD were purchased from Xi’an polymer light technology corp. Bis(trifluoromethane) sulfonamide lithium salt (Li-TFSI), and chlorobenzene were purchased from Sigma-Aldrich. Dimethylformamide (DMF), dimethyl sulfoxide (DMSO), isopropanol (IPA), acetonitrile, and diethyl ether were obtained from Acros Organics. Cobalt(III) FK209 TFSI Salt was received from Greatcell Solar Materials. The carbon paste was used as purchased from Dynano AB (Product reference DN-CP01).

Three-Dimensional Perovskite Precursor Solution: FAPbI₃ perovskite precursor solution was prepared by dissolving 206.4 mg of FAI, 575.3 mg of PbI₂, and 44.6 mg of MACI in a 1 mL of DMF and DMSO mixed solvent (8:1 v/v).

Fabrication of the Perovskite Devices: A Fluorine doped tin oxide (FTO) glass (Asahi FTO glass) was cleaned with detergent, deionized water, acetone, and IPA, sequentially. A hole blocking TiO₂ layer was deposited by spray pyrolysis of a solution of titanium (IV) disopropoxide bis(acetylacetonate) diluted in IPA (1:15, v/v) at 450 °C. A mesoporous TiO₂ layer was deposited by spin-coating at 1500 rpm for 40 s using a diluted TiO₂ paste (Sharechem, SC-HT040) in ethanol (0.112 g mL⁻¹). Then the substrate was sintered at 500 °C for 30 min. After sintering, the substrates were transferred into a glovebox to prepare the perovskite layer. The perovskite solution was spin-coated onto the m-TiO₂ layer at 1000 rpm for 10 s followed by 6000 rpm for 30 s. Diethyl ether was dropped on the spinning substrate during the second step of spin-coating. The substrates were put onto the hotplate and annealed at 150 °C for 13 min.

For preparing the spiro-OMeTAD solution, 70 mg of spiro-OMeTAD was dissolved in 896 µL of chlorobenzene, mixing with 28 µL of tBP, 16 µL of Li-TFSI solution (from 517 mg/mL dissolved in acetonitrile), and 13 µL of Co-TFSI solution (from 376 mg/mL dissolved in acetonitrile). 40 µL of spiro-OMeTAD solution was spin-coated on the perovskite layer at 4000 rpm for 20 s. For the gold counter electrode, gold was thermally evaporated.

The deposition of the low temperature carbon-electrode was conducted through first delineating the active area, this was done with the help of custom-made adhesive polyimide masks from Solaronix. The carbon paste was then blade coated at a blade carbon distance of 220 µm, then annealed at 120 °C for 20 min.

Octylammonium Iodide-Based Two-Dimensional Passivation: OAI solution was prepared by dissolving 10 mg of OAI in 1 mL of IPA. 100 µL of OAI solution was deposited on the perovskite substrate by spin-coating at 4000 rpm for 20 s, and then the substrate was annealed at 100 °C for 5 min.

Characterization: The scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) images were captured through a Zeiss Auriga 60 electron microscope.

Current-voltage measurements were conducted through a class A Xenon arc lamp light source under constant AM1.5 G illumination with a Keithley 2400 source meter. The aperture of the shadow mask used was 0.1 cm². The reverse scan was measured first from 1.1 to −0.1 V followed by the forward scan from −0.1 to 1.1 V at a scan rate of 20 mV s⁻¹. The protocol for the stabilized measurements in Figure S7 (Supporting Information) consisted of the short circuit current ($I_{SC}$), open-circuit voltage ($V_{OC}$), and power conversion efficiency (PCE) measurements
being carried out subsequently in the following order. First, the stabilized PCE was measured at a fixed bias voltage determined from the average voltage at the MPP ($V_{\text{MPP}}$) from the reverse and forward $J-V$ curves of each device. As such, the bias voltage was fixed at 837 mV for the 3D/2D device and at 747 mV for the 3D device. Afterward, the $I_{SC}$ was measured for 250 s, followed by the $V_{OC}$ measurement for 250 s. The steady-state PCE, $I_{SC}$ and $V_{OC}$ measurements were performed with an approximate delay of 1 min between each measurement.

The device operational stability was measured by tracking maximum power point (MPP) of the devices for 500 h. The devices were kept in a sealed container flushed with nitrogen under continuous light illumination of 100 mW cm$^{-2}$ which was constantly calibrated during the measurement by a reference Si-photodiode placed in the container. The devices were tested without encapsulation.

External quantum efficiency spectra were obtained through a Xenon lamp light chopped at 130 Hz and monochromator illuminated wavelength from 300 to 1200 nm. The measurements were recovered through a signal recovery Lock-in amplifier (Model 7265 DSP).

Photoluminescence spectroscopy was conducted using a Fluorolog-3 (Horiba Scientific) with an excitation source of 450 nm. UV-vis absorption was measured using PerkinElmer Spectrophotometer. X-ray diffraction was performed using Bruker D8 Advance diffractometer.

X-ray Photoelectron Spectroscopy and Ultraviolet Photoelectron Spectroscopy measurements of the perovskite films were conducted with a photoelectron spectrometer (Kratos Inc., AXIS-Ultra DLD) in collaboration with Korea Basic Science Institute (KBSI). A monochromatic Al-Kα line operating at 1486.6 eV was used for XPS, and He-I source (21.22 eV) was used for UPS.

μm Resolved Photoluminescence Spectroscopy (μPL) and Light Beam Induced Current (LBIC) were performed through a commercially available confocal Raman scanning microscope (Witec), which was used to focus a UV laser beam (355 nm) onto a sample that was scanned pixel by pixel. The laser spot size was ≈3 μm for the used objective lens with 10x magnification (images with scale bar 600 μm and LBIC images) and 300 nm for the objective lens with 100x magnification (images with scale bar 5 μm). The emitted PL signal was spectrally resolved by coupling it via a dichroic mirror to a Czerny–Turner type spectrometer and detecting the signal with a silicon CCD linear array detector. For LBIC measurements the same setup was used for scanning. With a low noise current amplifier, the current output of the cell can be measured at each scanning position (every 40 μm). The laser used for excitation was a 635 nm diode laser (Laser power ~1.5 μW).

Electrochemical impedance spectroscopy measurements were performed using an Ivium CompactStat device, at a frequency range of 1 MHz to 100 mHz at negative applied bias voltage, under 100 klux illumination.

$J_{SC}-V_{OC}$ measurements were performed using a calibrated solar simulator and light filters for different light intensities. The light intensity was checked for each change of filters using a calibrated silicon reference device. The data used was collected from steady-state measurements of both $V_{OC}$ and $I_{SC}$.

$V_{OC}$ decay measurements were recorded for 900 ms. A red LED light from Thorlabs of wavelength 635 nm was used to illuminate the cells. The devices were measured in a dark room and kept under constant illumination for light soaking before switching off the light to track $V_{OC}$ decay. PicoScope 5000 series was used to acquire the measurements.

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.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

2D perovskites, carbon electrodes, defect passivation, interface engineering, passivating contacts, perovskite solar cells

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