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# Spray-assisted deposition of a SnO<sub>2</sub> electron transport bilayer for efficient inkjet-printed perovskite solar cells†

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Developing an efficient electron transport layer (ETL) through structural modification is essential to produce high-performance perovskite solar cell (PSC) devices. Specifically, the ETL should exhibit low defects, high optical transparency, and charge selectivity for ideal electron transport. Herein, we demonstrate (i) the low-temperature fabrication of tin oxide (SnO<sub>2</sub>) ETLs with a bilayer structure, and (ii) inkjet-printing of triple-cation perovskite films. Through the combined use of spin-coating and spray deposition, the optimized SnO<sub>2</sub>-bilayer ETL shows a nano-granule-textured surface, noticeably fewer defects, and a cascade conduction band position with the inkjet-printed perovskite film. The champion PSC device, based on the SnO<sub>2</sub>-bilayer ETL and inkjet-printed perovskite film, recorded an outstanding power conversion efficiency (PCE) of ~16.9%, which is significantly higher than the device based on the conventional SnO<sub>2</sub> ETL (PCE ~14.8%). The improved photovoltaic performance of the SnO<sub>2</sub>-bilayer-based device arises mainly from more efficient charge transport and suppressed recombination at the ETL/perovskite interface. The SnO<sub>2</sub>-bilayer ETL and inkjet-printed perovskite films demonstrated herein can be potentially used for large-scale manufacturing of photovoltaic modules.

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## 1. Introduction

In recent years, the power conversion efficiency (PCE) of lab-scale perovskite solar cells (PSCs) has reached an astoundingly high value of 25.7% by virtue of structural and defect engineering.<sup>1</sup> Conventionally, the perovskite photoabsorber films in PSCs are deposited using one-step antisolvent or two-step sequential deposition methods, both of which rely heavily on the spin-coating process.<sup>2,3</sup> The well-known spin-coating technique relies on centrifugal forces to generate the necessary liquid-vapor interface for perovskite film deposition, and thus, it exhibits poor scalability and limits the commercialization potential of PSCs. Consequently, numerous deposition methods that offer low raw material utilization rates and high film uniformity, such as vacuum deposition,<sup>4</sup> spray deposition,<sup>5</sup> brush painting,<sup>6</sup> doctor-blade coating,<sup>37</sup> and inkjet printing,<sup>7</sup> have been explored for the large-scale preparation of

perovskite films. Among these methods, inkjet printing (IJP) is the most material-efficient technique because it offers high cost-effectiveness, high writing accuracy, and a near-unity material utilization ratio.<sup>8,9</sup> The IJP technique has been popular for fabricating large-area perovskite films with a precisely-controlled thickness and interface, yielding satisfactory performance in planar PSCs.<sup>10</sup> Currently, the highest PCE achieved by inkjet-printed perovskite solar cell (IJP-PSC) is 21.7%, based on the p-i-n type configuration.<sup>11</sup> The IJP technique also allowed the fabrication of PSC devices with all-inkjet-printed perovskite absorbers and charge extraction layers with a maximum PCE of 17.2%.<sup>7</sup> Li *et al.* successfully prepared a large-area PSC device using the IJP technique and achieved a PCE of 18.64%.<sup>12</sup> The overall performance of IJP-PSCs is converging upon the state-of-the-art values achieved by solution-processed PSCs.

In the initial phase of the investigation, TiO<sub>2</sub> as an electron transport layer (ETL) was commonly used in n-i-p structured PSCs owing to its outstanding electronic and optical properties.<sup>13,14</sup> Based on the use of the mesoscopic TiO<sub>2</sub> ETL and inkjet-printed MAPbI<sub>3</sub> perovskite, the PSC achieved a maximum PCE of 12.3%.<sup>15</sup> However, the high processing temperature (>450 °C), low conductivity, and vulnerability to photo-oxidation of the TiO<sub>2</sub> layer make it less desirable for long-term use in PSCs.<sup>13</sup> As a replacement for TiO<sub>2</sub>, low-temp-

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erature processable ( $<185\text{ }^{\circ}\text{C}$ ) ETLs such as  $\text{ZnO}$ ,<sup>16</sup>  $\text{WO}_3$ ,<sup>17</sup>  $\text{NbO}_x$ ,<sup>18</sup>  $\text{CeO}_x$ ,<sup>38</sup>  $\text{Fe}_2\text{O}_3$ ,<sup>19</sup> and  $\text{SiO}_2$ <sup>20–22</sup> were introduced and applied in PSCs. In particular,  $\text{SnO}_2$  has been investigated extensively due to its highly comparable optoelectronic properties with  $\text{TiO}_2$ , including high optical transparency and charge selectivity, excellent electron mobility ( $240\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ ), and more importantly, low-temperature processability.<sup>23</sup> Furthermore,  $\text{SnO}_2$  has a favorable energy level alignment with the commonly used  $\text{FAPbI}_3/\text{MAPbI}_3$  perovskites, *i.e.* having conduction and valence band edges below the perovskite absorber for efficient charge collection and blocking at the ETL/perovskite interfaces.<sup>23</sup>

In its pristine state, solution-processed  $\text{SnO}_2$  exhibits a defect-rich nature, which is undesirable for its role as the ETL. To reduce the defect states and enhance the energy band structure,  $\text{SnO}_2$  has been used in tandem with other metal oxides, such as  $\text{TiO}_2$ , to form a bilayer ETL for solution-processed PSC devices, resulting in improved charge extraction and a PCE of  $\sim 19.8\%$ .<sup>24</sup> Thereafter, an amorphous-crystalline  $\text{SnO}_2$ -bilayer with a unique morphology was developed using a low-temperature solution process, further boosting the PCE of PSCs to  $20.39\%$  by virtue of improved charge transfer at the  $\text{SnO}_2$ /perovskite interface.<sup>25</sup> These works have demonstrated the advantages of low-temperature processed bilayer ETLs which leads to the enhanced performance of solution-processed PSCs. In the current stage, the use of the  $\text{SnO}_2$  ETL is less popular for IJP-PSCs. Initially, a mesoporous  $\text{TiO}_2$  ETL and  $\text{FAMAPbBr}_3$  absorber were used to fabricate PSC devices, which showed a good PCE of  $14.11\%$ .<sup>26</sup> Also,  $\text{MAPbI}_3$  and  $\text{CsFAMAPb}(\text{Br}, \text{I})_3$ -based IJP-PSCs fabricated with  $\text{TiO}_2$  as the ETL have achieved maximum PCEs of  $18.20\%$  and  $19.60\%$ .<sup>12,27</sup> The IJP-PSC devices fabricated with modified compact and mesoporous  $\text{TiO}_2$  ETLs exhibited a PCE of  $9.1\%$ .<sup>28</sup> To the best of our knowledge, there is only one report demonstrating the use of an  $\text{SnO}_2$  ETL for IJP-PSCs, in which a PCE of  $10.35\%$  was achieved by incorporating polymer additives into the perovskites.<sup>29</sup> To improve the charge transfer without altering the optical properties of ETLs, the utilization of bilayer ETLs can be a successful strategy for enhancing the device performance of IJP-PSCs.

Here, we rationally designed a highly crystalline  $\text{SnO}_2$ -bilayer ETL *via* the combined use of spin-coating and spray-deposition approaches. Specifically, a  $\sim 30\text{ nm}$  thick  $\text{SnO}_2$  underlayer was first deposited on the substrate by spin-coating the sol-gel precursor, followed by the spray deposition of  $\text{SnO}_2$  colloidal solution to produce an overlaying scaffold layer. In this individual case, the spin-coated  $\text{SnO}_2$  (spin- $\text{SnO}_2$ ) film exhibits a smooth yet compact surface, whereas the spray-deposited  $\text{SnO}_2$  (spray- $\text{SnO}_2$ ) film has a mesoporous, nanograin-textured surface. Therefore, the resulting  $\text{SnO}_2$ -bilayer ETL can inherit the exceptional morphological features found in both spin- $\text{SnO}_2$  and spray- $\text{SnO}_2$  films. The characterization confirmed that the  $\text{SnO}_2$ -bilayer exhibits better morphology, reduced defects, and more suitable conduction and valence band alignments with the inkjet-printed perovskite layer than the commonly used spin- $\text{SnO}_2$ . The results show that the  $\text{SnO}_2$ -bilayer can prevent direct contact among the ITO/perovs-

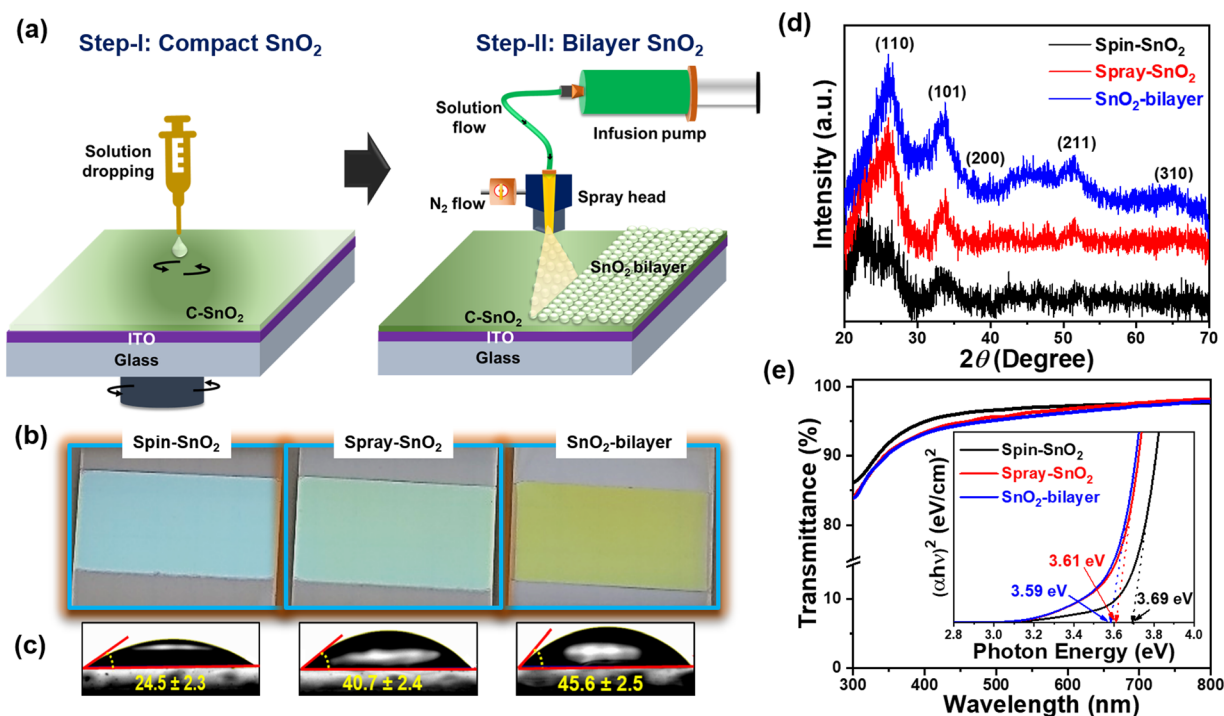
kite layers more effectively than the spin- $\text{SnO}_2$  and spray- $\text{SnO}_2$  ETLs. At the same time, the  $\text{SnO}_2$ -bilayer also exhibited a nano-granule-textured surface which produces larger surface-to-volume ratios as compared with spin- $\text{SnO}_2$  and spray- $\text{SnO}_2$  single-layer films, creating a maximum ETL/absorber interfacial area for efficient charge transport. Thus, the best  $\text{SnO}_2$ -bilayer-based IJP-PSC successfully attained a maximum PCE of  $16.9\%$ , and its significantly higher PCE is associated with the spin- $\text{SnO}_2$  based devices. The spray-assisted  $\text{SnO}_2$ -bilayer ETL developed herein can be potentially used to develop large-scale IJP-PSC devices with improved performance and durability.

## 2. Results and discussion

### 2.1 Structural, morphological, and optoelectronic properties of $\text{SnO}_2$ films

The  $\text{SnO}_2$ -bilayer ETL was fabricated using a two-step strategy, *i.e.* spin coating the sol-gel precursor solution and a spray deposition technique, as demonstrated in Fig. 1(a). The synthesis parameters for spray coating have been applied as mentioned in the previous literature<sup>21</sup> to produce high-quality  $\text{SnO}_2$  films. In the digital photographs of the spin- $\text{SnO}_2$ , spray- $\text{SnO}_2$ , and  $\text{SnO}_2$ -bilayer films shown in Fig. 1(b), the color of the  $\text{SnO}_2$ -bilayer film is more greenish than the spin and spray- $\text{SnO}_2$  films. Based on the water contact angle (WCA) profiles displayed in Fig. 1(c), the spray- $\text{SnO}_2$  ( $\theta \sim 41^\circ$ ) and  $\text{SnO}_2$ -bilayer ( $\theta \sim 46^\circ$ ) films showed more hydrophobic behavior than the spin- $\text{SnO}_2$  ( $\theta \sim 25^\circ$ ) film. As discussed in previous work,<sup>30</sup> the wettability of the substrate or ETL/HTL and the growth of perovskite grains are closely linked. Low-density nuclei are produced on the hydrophobic substrate in the initial nucleation step, and can further expand and coarsen to larger grains during the thermal annealing step. Fig. 1(d) displays the X-ray diffraction (XRD) patterns of the spin- $\text{SnO}_2$ , spray- $\text{SnO}_2$ , and  $\text{SnO}_2$ -bilayer films, broad diffraction peaks with lower intensity owing to the ultra-fine size ( $\sim 3\text{ nm}$ ) of  $\text{SnO}_2$ .<sup>21</sup> The diffraction peaks observed in all the three films at the  $2\theta$  values of  $26.6^\circ$ ,  $33.9^\circ$ ,  $38.8^\circ$ ,  $51.8^\circ$ , and  $65.91^\circ$  corresponding to the (110), (101), (200), (211), and (310) planes, respectively. These spectra match well with JCPDS no.: 01-072-1147, confirming the tetragonal crystal structure of tin oxide.<sup>21</sup>

The prepared spin- $\text{SnO}_2$ , spray- $\text{SnO}_2$ , and  $\text{SnO}_2$ -bilayer films over glass substrates were used for further studies. The transmittance spectra of all three  $\text{SnO}_2$  films were recorded using a UV-visible spectrometer and are shown in Fig. 1(e). The transmittance values at a wavelength of  $550\text{ nm}$  for spin- $\text{SnO}_2$ , spray- $\text{SnO}_2$ , and  $\text{SnO}_2$ -bilayer films are  $96.9\%$ ,  $96.3\%$ , and  $95.6\%$ , respectively, and this trend matches well with previous work.<sup>25</sup> The thickness (obtained from the surface profilometer) of the spin- $\text{SnO}_2$  is  $\sim 30\text{ nm}$ , and that of spray- $\text{SnO}_2$  is  $\sim 60\text{ nm}$ ,<sup>21,25</sup> whereas the thickness of the  $\text{SnO}_2$ -bilayer was quite increased with a value of  $\sim 80\text{ nm}$ . The reduction in the transmittance can be associated with the increased thickness of bilayer- $\text{SnO}_2$  films. The optical band gap ( $E_g$ ) of the different  $\text{SnO}_2$  ETLs was calculated from the Tauc plot (inset) in



**Fig. 1** (a) Schematic illustration of the fabrication process of  $\text{SnO}_2$ -bilayer films, (b) digital photographs of  $\text{SnO}_2$  films coated on patterned ITO substrates, (c) contact angles of water on spin- $\text{SnO}_2$ , spray- $\text{SnO}_2$ , and  $\text{SnO}_2$ -bilayer films, (d) XRD patterns, and (e) transmittance spectra and the Tauc plot (inset) of spin- $\text{SnO}_2$ , spray- $\text{SnO}_2$ , and  $\text{SnO}_2$ -bilayer films.

Fig. 1(e). The obtained  $E_g$  values for spin- $\text{SnO}_2$ , spray- $\text{SnO}_2$ , and  $\text{SnO}_2$ -bilayer films are  $\sim 3.69$  eV,  $\sim 3.61$  eV, and  $\sim 3.59$  eV, respectively. The small change in  $E_g$  is due to the substantial variation in the band alignment of the  $\text{SnO}_2$  resulting from surface texture upgradation.

The surface texture of the spin- $\text{SnO}_2$ , spray- $\text{SnO}_2$ , and  $\text{SnO}_2$ -bilayer films was investigated using a field-emission scanning electron microscope (FE-SEM). From the FE-SEM images in Fig. 2(a), the spin- $\text{SnO}_2$  film had a compact morphology, whereas the surfaces of spray- $\text{SnO}_2$  and  $\text{SnO}_2$ -bilayer films were covered with ultrafine granular structures. The average size of the nano-granules in the spray and  $\text{SnO}_2$ -bilayer films was  $\sim 40$  nm. These granules on the spray and  $\text{SnO}_2$ -bilayer film surfaces are also visible through atomic force microscopy (AFM) analysis. The micrographs shown in Fig. 2(b) reveal that these granules were absent on the surface of spin- $\text{SnO}_2$ , which confirms that it can be only formed during the *in situ* spray coating process.<sup>21</sup> Their nano-textured-granule structure, spray- $\text{SnO}_2$ , and  $\text{SnO}_2$ -bilayer films exhibited a slightly larger specific root-mean-square (RMS) roughness values of  $\sim 2.7$  nm and  $\sim 2.6$  nm compared with spin- $\text{SnO}_2$  (RMS  $\approx 2.1$  nm). These ultrafine granules give rise to a mesoporous morphology in the spray- $\text{SnO}_2$  and  $\text{SnO}_2$ -bilayer films, which can increase the contact area at the interface of the ETL/absorber for efficient charge collection.<sup>21,25</sup>

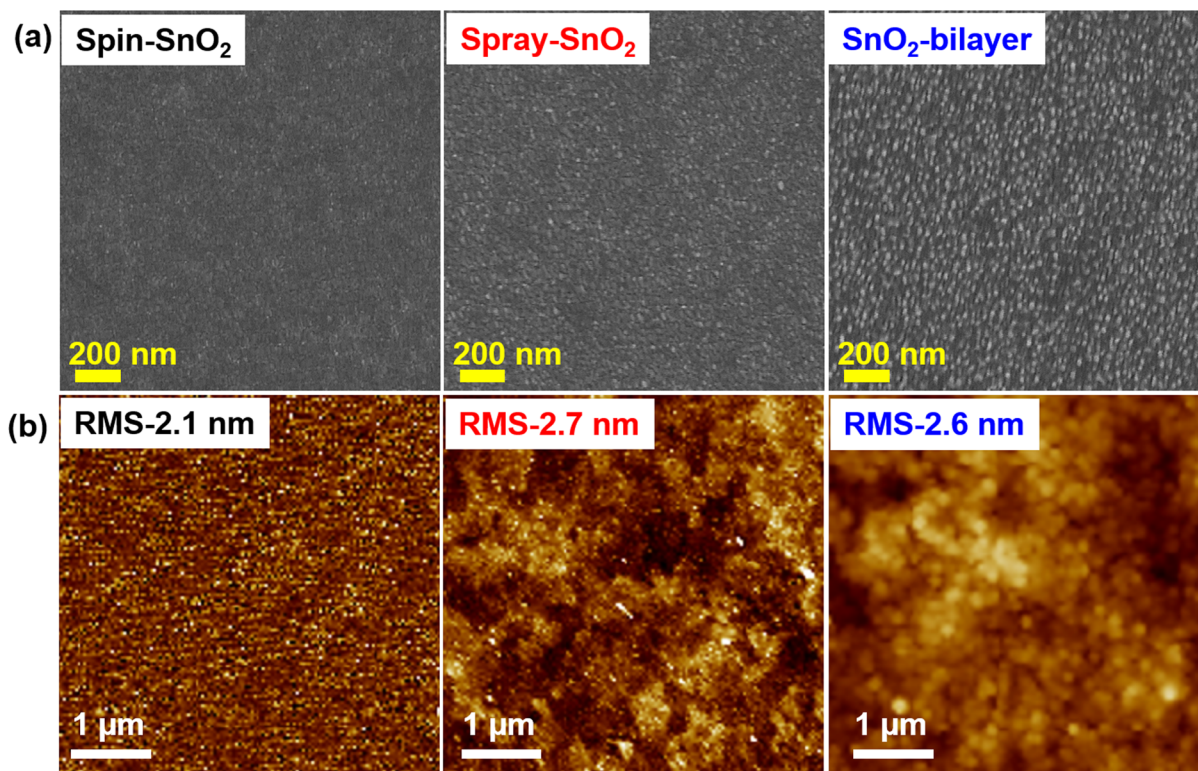
X-ray photoelectron microscopy (XPS) analysis was performed to study the surface elemental composition of the spin- $\text{SnO}_2$ , spray- $\text{SnO}_2$ , and  $\text{SnO}_2$ -bilayer films. Fig. 3a

describes that the O 1s core level spectra of three  $\text{SnO}_2$  films were elaborated into different oxygen components, namely  $\text{O}_1$ ,  $\text{O}_2$ , and  $\text{O}_3$ . Precisely, the major  $\text{O}_1$  peak situated at a lower binding energy (BE) of  $\approx 530$  eV is related to the lattice oxygen in the Sn-O, however, the minor  $\text{O}_2$  ( $\approx 531.5$  eV) and  $\text{O}_3$  ( $\approx 532.5$  eV) peaks are correlated with the oxygen vacancies ( $\text{V}_\text{O}$ ) and dangling hydroxyl ( $-\text{OH}$ ) groups confined in  $\text{SnO}_2$ , respectively.<sup>25,31</sup>

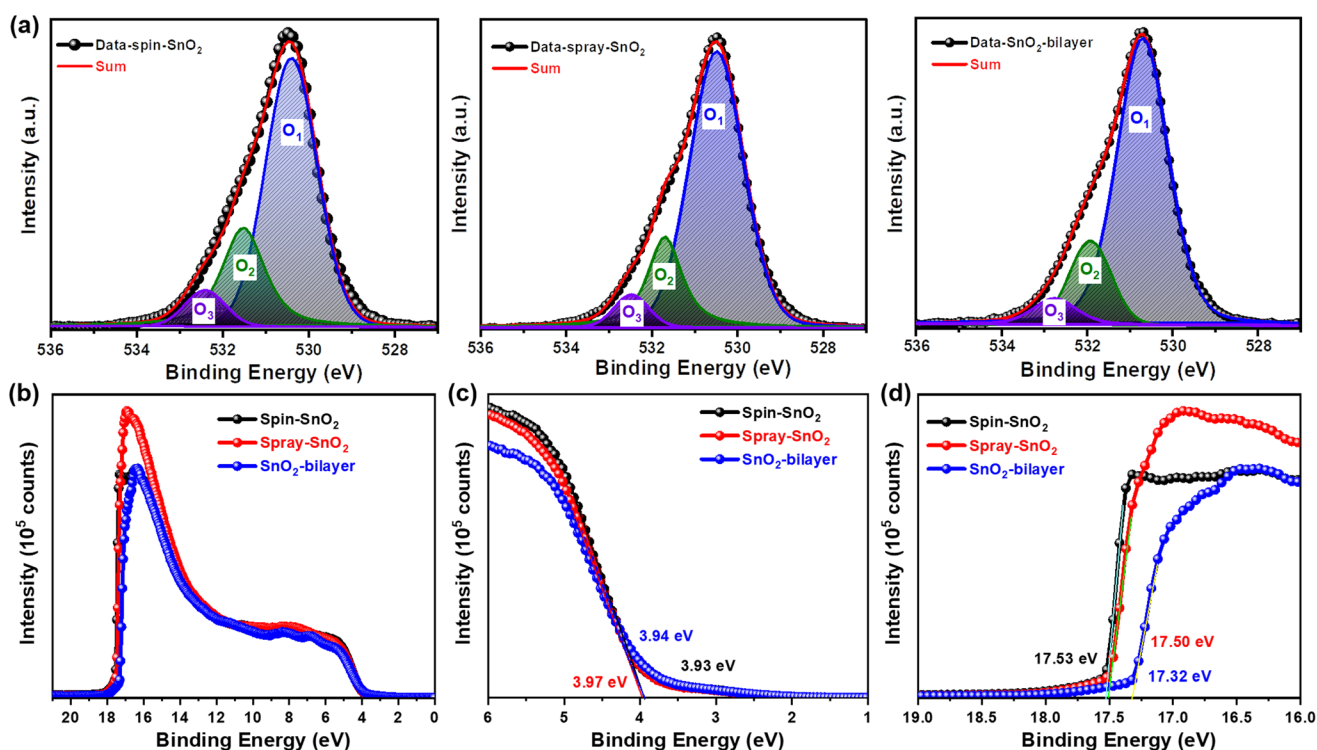
The amount of lattice ( $\text{O}_\text{lattice}$ ;  $\text{O}_1$ ) and defects ( $\text{O}_\text{defect}$ ;  $\text{O}_2 + \text{O}_3$ ) for oxygen atoms were estimated for all  $\text{SnO}_2$  films by calculating the area under the curve for every O component. In Table S1,<sup>†</sup> it is presented that the spin- $\text{SnO}_2$  film exhibited a larger  $[\text{O}_\text{defect}/\text{O}_\text{lattice}]$  fraction of  $\approx 0.41$ , indicating the abundance of oxygen-related defects in the spin- $\text{SnO}_2$  film surface acquired. In contrast, the  $\text{SnO}_2$ -bilayer film exhibited the lowest fraction of  $[\text{O}_\text{defect}/\text{O}_\text{lattice}] \approx 0.28$ , suggesting that the presence of very few oxygen defects and the O component originates mainly from Sn-O. A lower fraction  $[\text{O}_\text{defect}/\text{O}_\text{lattice}]$  of the  $\text{SnO}_2$ -bilayer film initiates mostly from the decrease of  $-\text{OH}$  groups ( $\text{O}_3$ ). The main reason for the dominant charge transport from the ETL/absorber interface can be related to these  $-\text{OH}$  groups and  $\text{V}_\text{O}$  defects which create recombination sites on the ETL surfaces. Hence, the knowingly fewer O-defects in the  $\text{SnO}_2$ -bilayer film are incredibly advantageous for charge transport in PSCs.

Alongside the XPS measurements, UPS measurements were conducted to investigate the energy band alignments of all  $\text{SnO}_2$  films. Fig. 3(b-d) present the UPS spectra of the  $\text{SnO}_2$





**Fig. 2** (a) Top-view FE-SEM images and (b) AFM micrographs depicting the surface morphologies and topographies of spin-SnO<sub>2</sub>, spray-SnO<sub>2</sub>, and SnO<sub>2</sub>-bilayer films.



**Fig. 3** (a) XPS spectra of the O 1s core level of different SnO<sub>2</sub> films (spin-SnO<sub>2</sub>, spray-SnO<sub>2</sub>, and SnO<sub>2</sub>-bilayer) on ITO glass. (b) Ultraviolet photoelectron spectroscopy (UPS) spectra, (c) on-set region, and (d) cut-off region of spin-SnO<sub>2</sub>, spray-SnO<sub>2</sub>, and SnO<sub>2</sub>-bilayer films.

films, cut-off edge, and valence band region. The values of  $E_{\text{cut-off}}$  and  $E_{\text{on-set}}$  were extracted from Fig. 3(c and d) for all  $\text{SnO}_2$  films and are summarized in Table S2.† Using Expression S1,† the work function ( $W_s$ ) values of the spin- $\text{SnO}_2$ , spray- $\text{SnO}_2$ , and  $\text{SnO}_2$ -bilayer films were estimated to be  $-3.69$ ,  $-3.72$ , and  $-3.90$  eV, respectively. Meanwhile, the valence band energy levels ( $E_{\text{VB}}$ ) of the spin- $\text{SnO}_2$ , spray- $\text{SnO}_2$ , and  $\text{SnO}_2$ -bilayer films were estimated as  $-7.62$ ,  $-7.69$ , and  $-7.84$  eV, individually (Expression S2†). The calculated conduction band energy level ( $E_{\text{CB}}$ ) values for the spin- $\text{SnO}_2$  ( $-4.04$  eV), spray- $\text{SnO}_2$  ( $-3.97$  eV), and  $\text{SnO}_2$ -bilayer ( $-4.11$  eV) films reveal the deeper  $E_{\text{CB}}$  of the  $\text{SnO}_2$ -bilayer could effectively transfer the electrons from the perovskite to  $\text{SnO}_2$ . In addition, the deeper  $E_{\text{VB}}$  of the spray- $\text{SnO}_2$  and  $\text{SnO}_2$ -bilayer than the spin- $\text{SnO}_2$  possibly will efficiently reduce bimolecular recombination at the  $\text{SnO}_2$ /absorber interface, which can improve the charge transport. The XPS and UPS outcomes taken together verify the alterations in the elemental composition and the exact energy band position of the  $\text{SnO}_2$ -bilayer ETL can contribute positively to the performance of inkjet-printed photovoltaic devices.

## 2.2 Structural, morphological, and optoelectronic properties of inkjet-printed perovskite films

Fig. 4(a) schematically illustrates the inkjet-printing process of triple-cation perovskite films on different  $\text{SnO}_2$  ETLs. The structural information and crystal phase of the resulting inkjet-printed  $\text{SnO}_2$ /perovskite films were analyzed using an X-ray diffractometer. Based on the XRD patterns in Fig. 4b, all of the perovskite films displayed a prominent peak corresponding to the (001) plane at a  $2\theta$  value of  $\sim 14.1^\circ$  regardless of the  $\text{SnO}_2$  underlayers. In addition to the (001) peak, other representative peaks such as (011), (111), (002), (012), (112), (022), and (003) were also detected, which can be indexed to the cubic crystal structure of the  $\text{CsFAMAPbBr}_{x-1}\text{I}_{3-x}$  perovskite.<sup>32,33</sup> Comparatively, the intensities of the (001) and (002) planes in the  $\text{SnO}_2$ -bilayer/perovskite film are relatively higher than those of the spin- $\text{SnO}_2$ /perovskite and spray- $\text{SnO}_2$ /perovskite samples, implying the superior crystallinity of the perovskite film in the former. A low-intensity subtle peak of the  $\delta$ -phase<sup>34</sup> perovskite was observed at  $11.78^\circ$  in all three samples, indicating the incomplete transformation of the

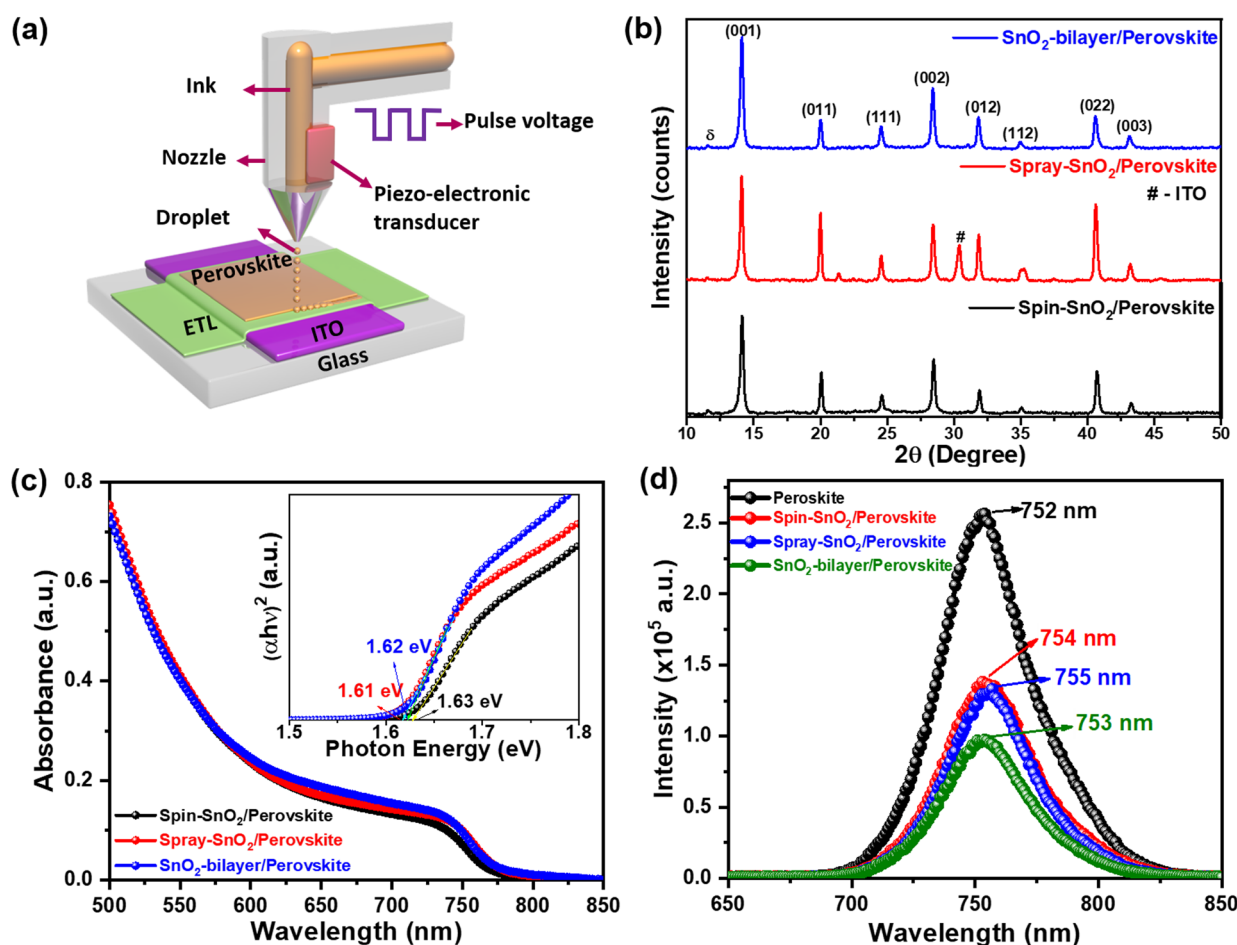


Fig. 4 (a) Schematic illustration of perovskite film fabrication using inkjet printing. (b) X-ray diffraction (XRD) patterns of inkjet-printed perovskite films fabricated on spin- $\text{SnO}_2$ , spray- $\text{SnO}_2$ , and  $\text{SnO}_2$ -bilayer ETLs. (c) UV-vis spectra and the Tauc plot (inset) of inkjet-printed perovskite films fabricated on spin, spray, and  $\text{SnO}_2$ -bilayer ETLs. (d) Steady-state photoluminescence (PL) spectra of inkjet-printed perovskite films fabricated on spin, spray, and  $\text{SnO}_2$ -bilayer ETLs.

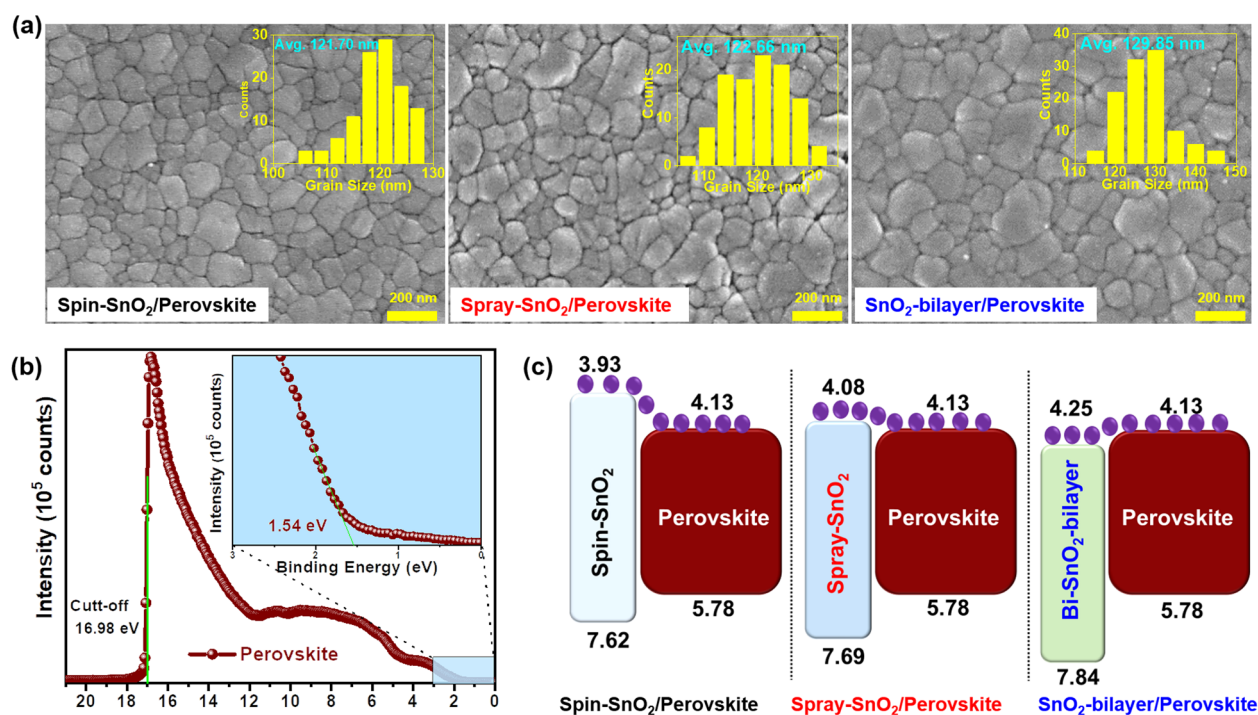
$\delta$ -phase (yellow) perovskite to the  $\alpha$ -phase (black) perovskite.<sup>32</sup> The  $\text{PbI}_2$  peak was not detected in all of the samples, indicating the formation of highly crystalline perovskite films over different  $\text{SnO}_2$  underlayers. The estimated crystallite sizes (Debye-Scherrer formula) for the spin- $\text{SnO}_2$ /perovskite, spray- $\text{SnO}_2$ /perovskite, and  $\text{SnO}_2$ -bilayer/perovskite samples were calculated to be  $\sim 34.5$  nm,  $36.4$  nm, and  $36.5$  nm, respectively.

Furthermore, all of the  $\text{SnO}_2$ /inkjet-printed perovskite films revealed an absorption edge in the region of 760–770 nm (Fig. 4c), and estimated values of  $E_g \approx 1.63$ – $1.61$  eV (inset). Simultaneously, steady-state photoluminescence (PL) results revealed the electron extraction dynamics at the  $\text{SnO}_2$ /perovskite interface, and the resulting PL spectra are displayed in Fig. 4(d). The reference inkjet-printed perovskite film showed pronounced PL emission that peaked at 752 nm. With the spin- $\text{SnO}_2$ , spray- $\text{SnO}_2$ , and  $\text{SnO}_2$ -bilayer ETLs, the inkjet-printed perovskite films showed quenching of the intensity by  $\sim 46\%$ ,  $\sim 47\%$ , and  $\sim 63\%$ , respectively. Apparently, the  $\text{SnO}_2$ -bilayer can extract the charge more efficiently than the other counterparts at the  $\text{SnO}_2$ /perovskite interface, as evident in its largest PL quench. This is because the  $\text{SnO}_2$ -bilayer exhibited a lower fraction of oxygen defects and  $-\text{OH}$  groups, which act as trap states. Moreover, the PL spectra also revealed a minor red-shift in the emission peak of the perovskite films using  $\text{SnO}_2$  ETLs, possibly due to the strain induced by lattice distortion.<sup>35</sup>

The FE-SEM images displayed in Fig. 5a revealed that all inkjet-printed perovskite samples are more compact, pinhole-

free, and made up of distinct grains. The grain size distributions of the various  $\text{SnO}_2$ /perovskite films were presented in histogram plots (insets). The  $\text{SnO}_2$ -bilayer/perovskite sample had an average grain size of  $\sim 130$  nm, which is larger than the spin- $\text{SnO}_2$ /perovskite ( $\sim 122$  nm) and spray- $\text{SnO}_2$ /perovskite ( $\sim 123$  nm) samples. The larger grain size is due to the hydrophobic nature of the  $\text{SnO}_2$  ETL layer, which correlates well with the wettability results of  $\text{SnO}_2$  ETLs discussed above. The cross-sectional FE-SEM images of the perovskite layers deposited over different  $\text{SnO}_2$  ETLs are shown in Fig. S1.† The average thickness values for spin- $\text{SnO}_2$ /perovskite, spray- $\text{SnO}_2$ /perovskite, and  $\text{SnO}_2$ -bilayer/perovskite samples were found to be  $\sim 405$ ,  $\sim 395$ , and  $\sim 398$  nm, respectively. The AFM micrographs (Fig. S1†) illustrate that the surface of the inkjet-printed perovskite films is denser, without pinholes/voids, and these results are more related to FE-SEM as discussed previously. The values of RMS roughness for the inkjet-printed perovskite film over the spin- $\text{SnO}_2$ , spray- $\text{SnO}_2$ , and  $\text{SnO}_2$ -bilayer ETLs was measured to be  $\sim 33$  nm,  $\sim 24$  nm and  $\sim 21$  nm, respectively. The uniform and smooth surface of the inkjet-printed perovskite films can be potentially used for the manufacturing of large-scale semitransparent photovoltaic devices.<sup>36</sup>

The core-level XPS spectra of Pb 4f, I 3d, Br 3d, C 1s, N 1s, and Cs 3d elements of the inkjet-printed perovskite film over glass substrate are shown in Fig. S2(a).† Generally, Pb 4f spectra consist of two high-intensity Pb 4f<sub>7/2</sub> and Pb 4f<sub>5/2</sub>



**Fig. 5** (a) Surface morphologies and grain size distributions (inset) of perovskite films inkjet-printed on different  $\text{SnO}_2$  ETLs. (b) Ultraviolet photoelectron spectroscopy (UPS) spectra of the perovskite film; the inset shows the onset region. (c) Schematic energy band alignment of inkjet-printed perovskite films with different  $\text{SnO}_2$  ETLs.



peaks that exist at BEs of 138.2 and 143.1 eV, respectively, with a spin-orbital splitting of 4.9 eV. The spectrum of I 3d shows two leading peaks at BEs of 619 and 630.5 eV. Fig. S2(b),† corresponding to the I 3d<sub>5/2</sub> and I 3d<sub>3/2</sub> components, individually. Fig. S2(c)† illustrates the two dominant peaks of the Br 3d core level spectrum at BEs of 68.3 and 69.2 eV belonging to the Br 3d<sub>5/2</sub> and Br 3d<sub>3/2</sub>, respectively. Similarly, the C 1s and N 1s core-level spectra in Fig. S2(d) and (e)† depict the C=NH<sub>2</sub><sup>+</sup> at 288.04 and 400.28 eV, respectively. The Cs 3d spectrum in Fig. S2(f)† represents the intensity of the Cs 3d<sub>5/2</sub> and Cs 3d<sub>3/2</sub> core levels at 724.5 eV and 738.53 eV, respectively. These results confirmed that the inkjet-printed perovskite film has high phase purity.

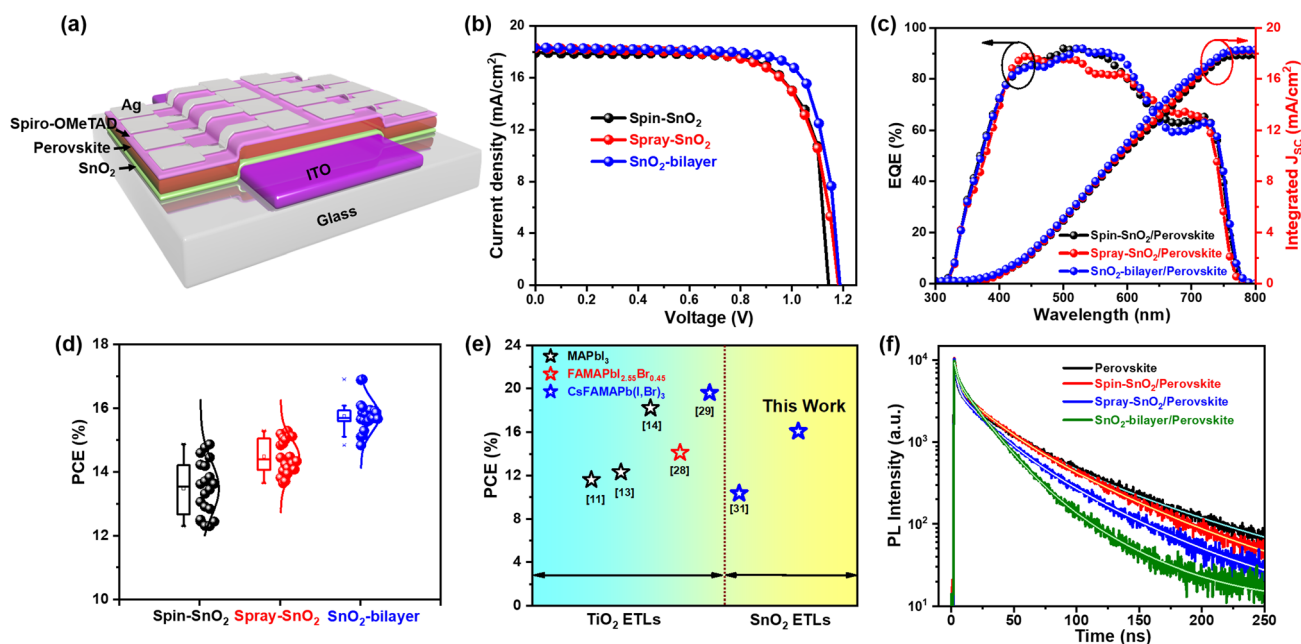
The  $E_{\text{cut-off}}$  and  $E_{\text{on-set}}$  values of the inkjet-printed perovskite film are investigated *via* UPS measurements. The values of work function ( $W_s$ ), as well as the valence band maximum ( $E_{\text{VB}}$ ) of the inkjet-printed perovskite film, were estimated from Fig. 5b and using Exp. S(1 and 2).† The conduction band maximum ( $E_{\text{CB}}$ ) and band gap values were estimated from Exp. S3† and the Tauc plot, respectively. All these parameters are summarized in Table S2.† The results revealed that the  $E_{\text{CB}}$  of the SnO<sub>2</sub>-bilayer ETL had a smaller band offset with the  $E_{\text{CB}}$  of the perovskite film, which is more beneficial for collecting charges at the SnO<sub>2</sub>/perovskite interface (Fig. 5c). Meanwhile, an energy barrier of ~0.05 eV was seen in the  $E_{\text{CB}}$  value of the spray-SnO<sub>2</sub> ETL and the  $E_{\text{CB}}$  value of the perovskite film, which can impede the interfacial electron transfer. The biggest band offset was observed in the spin-SnO<sub>2</sub>/perovskite interface, which can cause interfacial recombination of charge carriers and reduce the overall device performance. In addition, the

deeper  $E_{\text{VB}}$  value of the SnO<sub>2</sub>-bilayer compared to the spin-SnO<sub>2</sub> and spray-SnO<sub>2</sub> ETLs can help to inhibit recombination at the SnO<sub>2</sub>/perovskite boundaries, thereby improving the device performance of IJP-PSCs. Overall, these results have confirmed that significant variations have arisen in the elemental composition and band alignment of the SnO<sub>2</sub>-bilayer/perovskite film, which can lead to considerable changes in the device performance of PSCs.

### 2.3 Device performance of IJP-PSCs based on different SnO<sub>2</sub> ETLs

To investigate the device performance of SnO<sub>2</sub> ETLs, we fabricated *n-i-p* type IJP-PSCs with a device configuration of ITO/SnO<sub>2</sub>/inkjet-printed perovskite/spiro-OMeTAD/Ag, as schematically illustrated in Fig. 6(a). Fig. 6(b) displays the current density and voltage ( $J-V$ ) curves of the representative IJP-PSC devices fabricated on spin-SnO<sub>2</sub>, spray-SnO<sub>2</sub>, and SnO<sub>2</sub>-bilayer ETLs, and the detailed device parameters are presented in Table 1.

Based on the use of a similar inkjet-printed perovskite film, the device made up of a SnO<sub>2</sub>-bilayer ETL attained a notably better PCE of ~16.9% compared to the devices based on spin-SnO<sub>2</sub> (PCE ~14.8%) and spray-SnO<sub>2</sub> (PCE ~15.3%) ETLs. The superior performance of the SnO<sub>2</sub>-bilayer-based IJP-PSCs is mostly related to the efficient charge transfer between the SnO<sub>2</sub>/perovskite layers. Suitable band alignment and improved charge transfer at the ETL/perovskite interface can enhance the  $V_{\text{oc}}$  and FF of the device. SnO<sub>2</sub>-bilayer-based devices recorded a higher FF of 77.73% compared to those based on spin-SnO<sub>2</sub> (FF: 70.56%) and spray-SnO<sub>2</sub> (FF: 70.64%). A similar



**Fig. 6** (a) Schematic device architecture of a complete PSC device. (b)  $J-V$  characteristic curves, (c) EQE spectra and integrated photocurrent density of PSC devices based on different SnO<sub>2</sub> ETLs and inkjet-printed perovskite films. (d) PCE distributions of inkjet-printed PSCs based on different SnO<sub>2</sub> ETLs. (e) Comparison of the performance of state-of-the-art IJP-PSCs based on TiO<sub>2</sub> and SnO<sub>2</sub> ETLs. (f) TRPL spectra of inkjet-printed perovskite films coated on different SnO<sub>2</sub> ETLs.

**Table 1** Photovoltaic performance of inkjet-printed PSCs based on different SnO<sub>2</sub> ETLs

Device	$V_{oc}$ [V]	$J_{sc}$ [mA cm <sup>-2</sup> ]	$J_{sc}$ (EQE) [mA cm <sup>-2</sup> ]	FF [%]	PCE [%]	Avg. PCE [%]
Spin-SnO <sub>2</sub>	1.168	17.92	17.89	70.56	14.77	13.48 ± 0.8
Spray-SnO <sub>2</sub>	1.182	18.31	18.21	70.64	15.29	14.49 ± 0.5
SnO <sub>2</sub> -bilayer	1.187	18.32	18.30	77.73	16.90	15.76 ± 0.5

improvement was observed in the  $V_{oc}$  of the SnO<sub>2</sub>-bilayer-based device ( $V_{oc}$ : 1.187 V) compared to the devices based on spin-SnO<sub>2</sub> ( $V_{oc}$ : 1.168 V) and spray-SnO<sub>2</sub> ( $V_{oc}$ : 1.182 V). The higher  $V_{oc}$  of the SnO<sub>2</sub>-bilayer-based device is attributable to the deeper  $E_{VB}$  of the SnO<sub>2</sub>-bilayer ETL relative to those of the spin-SnO<sub>2</sub> and spray-SnO<sub>2</sub> ETLs. Overall, in the literature, the PCE of our IJP-PSC devices is the highest amongst the SnO<sub>2</sub>-based inkjet-printed PSC systems, as shown in Fig. 6(e).<sup>10,12,13,26,27,29</sup> The literature survey of the performance of IJP-PSC photovoltaic devices based on different TiO<sub>2</sub> and SnO<sub>2</sub> ETLs is presented in Table S5.† To provide further insight, electro-optical characterization was performed on IJP-PSC devices. The integrated  $J_{sc}$  values of the devices were estimated from the external quantum efficiency (EQE) spectra in Fig. 6(c). The device based on the SnO<sub>2</sub>-bilayer exhibited an integrated  $J_{sc}$  value of 18.30 mA cm<sup>-2</sup>, which matches well with the measured  $J_{sc}$  values obtained from the  $J$ - $V$  measurement (Table 1). On another note, we also investigated the long-term stability and photostability of IJP-PSC devices comprising different SnO<sub>2</sub>. The photostability measurements showed that all three devices generated stable  $J_{sc}$  values over a prolonged one-sun illumination for 500 s (Fig. S5(a)†). Nonetheless, the shelf-life of the IJP-PSCs based on spin-SnO<sub>2</sub> and spray-SnO<sub>2</sub> was lower than the analogues based on the SnO<sub>2</sub>-bilayer (Fig. S5(b)†). Moreover, the performance of 20 IJP-PSC devices with different SnO<sub>2</sub> ETLs was tested, and confirmed reproducibility data were displayed in a PCE distribution plot in Fig. 6(d). Among all, IJP-PSCs based on the SnO<sub>2</sub>-bilayer ETL achieved the highest average PCE of (15.76 ± 0.5)%, which clearly shows the highly reproducible performance of the devices. The  $J$ - $V$  curves of IJP-PSC devices under forward-scan and reverse-scan are shown in Fig. S4,† and the hysteresis index (HI) of every device was calculated using Expression S4.† The IJP-PSC device made with a SnO<sub>2</sub>-bilayer showed a considerably lower HI (~0.001) compared with the spin-SnO<sub>2</sub> (~0.012) and spray-SnO<sub>2</sub> (~0.007), and these low HI values were attributed to the improved SnO<sub>2</sub> ETL/perovskite interfacial morphology.<sup>25</sup> Furthermore, we fabricated normal PSC devices based on spin-coated perovskite films and tested them under similar conditions. The forward and reverse scan  $J$ - $V$  curves are depicted in Fig. S3,† and estimated  $J$ - $V$  parameters are described in Table S3.† Using the same SnO<sub>2</sub>-bilayer ETL, the PCE of the inkjet-printed PSC device (~16.9%) only showed an ~0.3% PCE decrease from that of the spin-coated PSC (PCE ~17.2%). Meanwhile, the devices made with spin-SnO<sub>2</sub> and spray-SnO<sub>2</sub> showed considerably larger PCE deficit values of ~2.4% and ~1.9%. This finding shows that the SnO<sub>2</sub>-

bilayer is a better ETL for IJP-PSCs, and it can also be flexibly used in solution-processed PSCs with different perovskite systems to produce good performance.

To study the charge transport properties between the SnO<sub>2</sub> ETL and the inkjet-printed perovskite absorber, we performed transient photoluminescence (TRPL) measurements on the SnO<sub>2</sub>/perovskite films, and the fluorescence decay lifetimes ( $\tau_{PL}$ ) of the samples were estimated using Expression S5†. As presented in Fig. 6(f), the reference inkjet-printed perovskite film (without SnO<sub>2</sub>) showed the maximum  $\tau_{PL}$  of 54 ns. With the incorporation of SnO<sub>2</sub>-bilayer, the  $\tau_{PL}$  values of the inkjet-printed perovskite film decreased to 25 ns (Table S4†), signifying a highly effective charge transfer at the SnO<sub>2</sub>/perovskite interface that contributed positively to the device performance of IJP-PSCs.

### 3. Conclusion

In summary, we have successfully developed SnO<sub>2</sub>-bilayer ETLs with better uniformity and a granule-textured surface using a solution-processed spin/spray-coating technique. The SnO<sub>2</sub>-bilayer ETL displayed a pinhole free nanograin-textured surface that benefitted the printing of the larger grain perovskite overlayer compared with spin-SnO<sub>2</sub> and spray-SnO<sub>2</sub> films. The device performance of SnO<sub>2</sub>-bilayer and spray-SnO<sub>2</sub> ETLs was investigated using the spin-SnO<sub>2</sub> ETL as a reference. The IJP-PSCs made with the SnO<sub>2</sub>-bilayer ETL and inkjet-printed perovskite film exhibited superior performance with a PCE of ~16.9%, compared to those of the spin-SnO<sub>2</sub> (PCE ~14.8%) and spray-SnO<sub>2</sub> (~15.3%) analogues. The spray-assisted deposition of SnO<sub>2</sub> ETLs and the inkjet-printing of perovskite films under ambient conditions enable the production of large-area photovoltaic devices/modules that are entirely compatible with roll-to-roll (R2R) processing over rigid/flexible electrodes.

### Author contributions

V. V. S.: conceptualization, visualization, methodology, formal analysis, investigation, and writing – original draft, review and editing. N. K.: methodology, supervision and writing – review and editing. H. B. L.: supervision and writing – review and editing. M. M. O.: methodology, writing – review and editing, and formal analysis. S. C.: methodology and formal analysis. B. T.: methodology and formal analysis. A. M.: formal analysis. J.-W. K.: supervision, funding acquisition, and writing – review and editing.

### Conflicts of interest

The authors declare no conflict of interest.

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