## Supporting Information

# Blade Printing of Low-Melting-Point-Alloys as Back Electrodes for High-Efficiency and Stable Inverted Perovskite Solar Cells

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#### **Experimental methods**

#### Materials:

All the solvents including N,N-Dimethylformamide (DMF, 99.99%, J&K), N-Methylpyrrolidone (NMP, 99.9%, J&K), isopropanol (IPA, 99.5%, J&K), chlorobenzene (CB, 99.9%, J&K) were used as received without further purification. Cesium iodide(CsI, 99.99%, Advanced Eletion Technology Co., Ltd), Formamidine Hydroiodide(FAI), Lead(II) iodide(PbI<sub>2</sub>), Lead chloride(PbCl<sub>2</sub>, 99.99%, Advanced Eletion Technology Co., Ltd), (4-(7H-dibenzo[c,g]carbazol-7-yl)butyl)phosphoni acid(4PADCB), Poly[bis(4-phenyl)(2,4,6-triMethylphenyl)aMine](PTAA), were bougut from TCI(Japan). BCP(99.9%) and C60(99.9%) were bought from Xi'an Polymer Light Technology Corp(China).

#### **Precursor Preparation:**

As an example, for the preparation of the  $FA_{0.83}C_{s0.17}PbI_3/DMF$  solution containing 10% PbCl<sub>2</sub> and NMP: 142.8 mg of FAI, 44.2 mg of CsI, 461 mg of PbI<sub>2</sub>, 27.8 mg of PbCl<sub>2</sub>, and 96 µL of NMP are dissolved in 500 µL of DMF to obtain the precursor solution. To facilitate dissolution, the resulting precursor solution can be heated and stirred at 70°C for two hours.

#### **Device fabrication:**

The patterned ITO glass (10  $\Omega$ /sq, 1.5×1.5 cm) was washed by sonication with deionized water, acetone and isopropanol for 10 min. Then, the ITO glasses were cleaned by a UV-ozone cleaner for 20 min followed by spin coating 40 µL 4PADCB as hole-transporting layer (HTL). The HTL-coated substrates were heated to 100 °C, followed by spin-coating perovskite solution at the speed of 5000 rpm for 50 s without the assistance of antisolvent. The perovskite films were annealed at 150 °C for 10 min. Then, C<sub>60</sub> of 40 nm and BCP of 8 nm were thermally evaporated under vacuum of 4×10<sup>-5</sup> Torr at the rate of 0.2 Å/s. For reference devices, Cu or Ag of 100 nm were thermally evaporated under vacuum of 4×10<sup>-5</sup> Torr at the rate of 0.2 Å/s.

LMPA electrodes were fabricated using the flexible blade-coating apparatus provided by CrystalSpray Technology (Shenzhen) Co., Ltd (<u>http://www.crystal-</u> spray.com/). LMPA electrodes were blade-coated on the ITO/4PADCB/perovskite/C<sub>60</sub>/BCP half-cell with the speed of 5 mm/s on the substrate at 68 °C, 90 °C, and 135 °C for the LMPAs with melting points of 62 °C, 80 °C, and 120 °C, respectively. The half-cell was fixed on a platform by the heated vacuum chuck. A 50  $\mu$ m-thick Tungsten mask with striped openings of 4.6 mm×1.6 mm was placed on the half-cell to pattern the electrodes. A flexible blade of polytetrafluoroethylene (PTFE) is used to coat the molten FM on top of the half cells. As the blade move pass and the half-cell, molten LMPA lamellas are created. Then the samples are removed from the heated platform to allow the LMPA films to solidify. The area of each LMPA, Cu and Ag electrodes is 0.074 cm<sup>2</sup>.

#### Characterization:

The optical microscopic images were measured by a white light interferometer (Z20, Zeta instruments). The SEM images were obtained by the scanning electron microscope (SU8230, Hitachi). The XRD spectra were measured with an D8 Advanc ECO X-ray Diffractometer using Cu Kα radiation under operating conditions of 25 kV and 15 mA from 0° to 55°. The XPS was measured by Escalab Xi+ X-ray photoelectron spectroscopy. Time-resolved photoluminescence (TRPL) decay transients were measured at 780 nm using excitation with a 478 nm light pulse from an Edinburgh FLS980 fluorimeter. The transient photoelectric streamer voltage measurement system (SouthPort SP-TPVC). The electrochemical impedance spectroscopy (EIS) was measured using an electrochemical workstation (CHI660E), under dark conditions with a bias voltage of 0.82 V.

The photovoltaic performance was measured in a nitrogen glove box. The current-voltage (*J-V*) characteristics were conducted using a Keithley 2400 source under AM 1.5 G solar illumination at 100 mW/cm<sup>2</sup>. The solar simulator system (Enlitech) satisfied the class AAA guidelines. The intensity of the solar simulator was calibrated by a standard silicon reference cell (Enlitech). The external quantum efficiency (EQE) spectra were recorded by a commercial EQE measurement system (QE-R3011, Enlitech). The EQE was measured by a DSR100UV-B spectrometer with a SR830 lock-in amplifier.

To minimize area errors caused by edge effects and ensure consistency in the measured area, we adopted a two-step mask strategy to define the PSC device area, as shown in Figure S2: 1) Printing mask: during the LMPA electrode printing process, a 50 µm-thick Tungsten mask with etched openings was used to define a slightly larger electrode region  $A_p \approx 0.12 \text{ cm}^2$ ; 2) Light mask: for *J-V* and EQE measurements, an optical aperture mask with an opening of 1.6 mm × 4.6 mm ( $A_L \approx 0.074 \text{ cm}^2$ ) was used to define the device area. This mask ensures that only the central region is illuminated, eliminating potential errors at the electrode edges.

To assess the impact of substrate temperature during LMPA electrode printing on device performance, we conducted a reference test by annealing vacuum-deposited electrode samples under the same temperature and duration conditions. The printing temperatures were 85°C and 120°C for the 80°C and 120°C LMPAs, respectively, with a heating duration of ~1 minute. Devices with vacuum-deposited Cu electrodes were first tested at room temperature, then heated on hot plates at 85°C and 125°C for 1 minute, respectively. After cooling to a stable state, *J-V* tests were repeated. The results, shown in Figure S5, indicate minimal changes in device performance parameters before and after annealing. This suggests that the brief annealing during LMPA printing has negligible effects on overall device performance.



Figure S1. Photograph of the printing apparatus



Figure S2. Schematic of the two-step mask strategy to define the PSC device area.



Figure S3. The UV photoelectron spectroscopy measurements for In-Sn-Bi alloys with melting points of (a) 62°C, (b) 80°C, and (c) 120°C, indicating work functions of 3.87, 3.77, and 3.72 eV, respectively.

Table S1 Properties of In-Sn-Bi alloys								
Melting point (°C)	In (Wt.%)	Sn (Wt.%)	Bi (Wt.%)	Work function (eV)	Crystal structure			
62	51	32.5	16.5	3.77	Eutectic			
80	29.68	16.3	54.02	3.75	Eutectic			
120	52	48	0	3.72	Eutectic			

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Materials	Melting point (°C)	Price (\$/kg)	Young's modulus (Gpa)	Thermal conductivity (W/(m·K))	Electrical conductivity (S/m)			
In	156.6	367	11	38.6	$1.2 \times 10^7$			
Sn	231.9	39	55	27.2	9.1 × 10 <sup>6</sup>			
Bi	271.4	15	32	12.5	$0.77  imes 10^6$			

Table S2 Properties of In, Sn, and Bi<sup>1</sup>

Table S3. Reported PCEs of PSCs adopting evaporation-free rear electrodes.

Years	Structures Electrodes		Technologies	PCE (%)	Refs
This work		Low-melting point alloys	Doctor-blading	22.46%	This work
2023.12		GaLMs	Doctor-blading	9%	2
2020.07	P-i-n	Ag NWs	Spray	13.11%	3
2020.06		Carbon	Doctor-blading	15.18%	4
2019.11		Ag NPs	Soaking	10%	5
2024.12		Carbon	hot pressing	20.31%	6
2024.07		Carbon	Doctor-blading	20.41%	7
2024.06		Carbon	High-pressure isostatic lamination	20.8%	8
2024.06		Carbon	Doctor-blading	20.08%	9
2024.03		Carbon	Doctor-blading	22.2%	10
2023.08		Carbon	Doctor-blading	19.2%	11
2023.07	N-i-p	Ni/graphite/Bi-In alloy	Doctor-blading	21.00%	12
2022.05		Graphene	Spray	22.07%	13
2020.06		Carbon black	Spray	12.48%	14
2020.03		Graphite paper/carbon film	Hot pressing	17.02%	15
2019.10		Graphite	Doctor-blading	18.10%	16
2019.01		NiO@carbon spheres	Hot pressing	11.70%	17
2018.04		Carbon	Doctor-blading	14.04%	18



Figure S4. Statistical photovoltaic parameters (VOC, JSC, FF, and PCE) PSCs with 62°C, 80°C, 120°C-LMPA, and Cu as electrodes.



Figure S5. *J-V* curves and performance parameters of Cu-electrode PSCs before and after annealing at 85°C and 125°C for 1 minute, respectively.



Figure S6. *J-V* curves and performance parameters of PSCs with areas of 0.1, 0.2 and 0.4 cm<sup>2</sup>. The electrode is printed using the 80°C LMPA.



Figure S7. The pinhole defects caused by shrinkage of the LMPA surface during the phase transition from liquid to solid.



Figure S8. Elemental distribution measured by ToF-SIMS for the perovskite layer by removing the alloy electrode from a PSC device after 300 hours of being kept in the air.



Figure S9. The optical microscopic images of electrode edges recorded during 1000 h. Edge of the electrode in contact with the BCP layer is on the left side in each picture.



Figure S10. The X-ray Photoelectron Spectroscopy (XPS) of In, Sn, and Bi in (a) fresh LMPA film, and (b) LMPA film aged in air for 300 hours.



Figure S11. Optical microscopical images of PSC surfaces after aging of 300 h: (a) with  $BCP/C_{60}$  and the LMPA electrode, (b) with  $BCP/C_{60}$  after removing the LMPA electrode, and (c) without the  $BCP/C_{60}$  layer.



Figure S12. Normalized PCE of 62°C LMPA-electrode PSC heated under the temperature of 85°C in N2 glovebox.



Figure S13. Schematic of LMPA electrodes recycling procedure.

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