Roll-to-Roll Slot-Die Coating of PTAA with PEDOT:PSS Buffer Layer for Perovskite Solar Cells: Insights from XPS Mapping

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1. Experimental Methods

1.1 Ink Preparation

To apply the buffer layer, the PEDOT:PSS (AI4083 from Ossila) was diluted in a 1:6 ratio with iso-propyl alcohol (IPA). This diluted solution was utilized for both spin coating and R2R slot die coating processes. For spin coating of PTAA, a solution was prepared by dissolving 2.5 mgml⁻¹ of PTAA (Sigma Aldrich) in toluene (Sigma Aldrich). As for R2R slot die coating, a solution containing 1 mgml⁻¹ of PTAA in toluene was used. 0.5 M MAPbl₃ ink is prepared by mixing 0.5 M MAI (Greatcell Materials) and 0.53 M Pbl₂ (TCI) with 6% excess Pb in methylamine solution with acetonitrile (TCI). The solution was stirred till the precursors dissolved. To make PCBM ink, 40mgml⁻¹ of PC61BM (Ossila) was dissolved in chlorobenzene and kept at 80°C for dissolution for two hours. For BCP, 0.5mgml⁻¹ of BCP (TCI) was dissolved in absolute ethanol.

1.2 Device Fabrication Methods

1.2.1 Spin Coated Device

For the devices with buffer layer deposition of PEDOT:PSS the prepared ink was spun via a two step process. First the film was spun at 1000RPM for 5 secs followed by 5000RPM for 15 secs. The buffer layer was then dried at 120°C for 10 minutes on a hot plate. This was followed by the PTAA deposition at 4000RPM for 30sec and dried at 100°C for 10 mins. The prepared MAPbl₃ ink is then spun on the PTAA layer at 2000 RPM for 60 seconds and dried for 10 minutes at 110°C. Next, a PCBM layer is deposited at 3000 RPM for 30 seconds with no external drying. A BCP layer is then deposited at 7000 RPM for 10 seconds. Finally, a 100 nm thick Ag electrode is thermally evaporated on top of the BCP layer to complete the device architecture. All the steps except thermal deposition were done in class 7 clean room at 25%RH.

1.2.2 R2R Slot Die Coating of PTAA and Buffer Layer

R2R slot die coating was dome Coatema smart coater (SC08). The smart coater contains two step inline convection oven with a total length of 1 m. For the coating of the buffer layer of PEDOT:PSS, the as-prepared ink solution was fed through the slot die head at optimised 0.72mlmin⁻¹(adjusted for changing the coating thickness). The coating width was defined by a 90 mm shim a 250 μ m tab width meniscus guide was used to control the meniscus. The gap between the slot die head and substrate was kept at 500 μ m including the tab width of the meniscus guide. The coating was done at 1 mmin⁻¹ and the wet film was dried at a set temperature of 140°C for both ovens. The roll was then rewound to coat PTAA on top of the buffer layer. 1mgml⁻¹ PTTA ink was used to deposit the PTAA layer. 1000 μ m tab width meniscus guide was used along with a 90mm wide shim to define the coating width. The pump rate was set at optimised 0.9mlmin⁻¹ to achieve 10 μ m wet film thickness. The wet film was then dried at a set temperature of 120°C for both ovens.

All the coatings in this study were deposited on a 5-meter-long, 10 cm-wide substrate using the Roll-to-Roll process. To ensure that our coating process accurately represents manufacturing conditions, samples were taken only after the coating had reached a steady-state deposition, typically after the first few meters of the process.

For a more representative and consistent analysis of film properties and device performance, we extracted three 28 mm × 28 mm samples from different positions across the width of the substrate—left, centre, and right. This approach, along length and width, allows us to assess the uniformity and performance of the coated films across the larger substrate while maintaining a practical device size for testing and characterisation.

The coated substrate was then taken offline and diced into 28x28mm² pieces, and the rest of the layers were coated following the coating procedure mentioned in the previous section.

1.3 Characterisation

JV measurement was done using a Keithley 2400 source meter. AAA rate solar simulator from Newport (oriel Sol3A) was used as the light source which was calibrated to 1 sun using a reference photodiode fitted with KG5 filter. The scan rate was set at $0.15Vs^{-1}$. The devices were masked with $0.09cm^2$ to define the active area. Light intensity dependent V_{oc} measurement was done using the same setup. The light intensity was controlled using neutral density filter. EQE measurement was used for the PL and EL measurement. For EL measurement an integrating sphere was used and Keithley source meter was used to apply external voltage. For SEM imaging JEOL JSM-7800F system was used.

XPS

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XPS was performed on a Kratos Axis Supra instrument using a monochomrated Al K α x-ray source with 15 mA emission current and 225 W power. The conductive substrate negated the need for charge neutralisation and no subsequent charge correction was required, with raw carbon spectra giving a primary peak at 284.8 eV (PET-ITO-PEDOT:PSS), or 284.5 eV (PET-ITO-PTAA). A single survey scan with a pass energy of 160 eV was collected for each sample to confirm the elements present on the surface. Subsequently spectra were collected in a grid pattern in order to generate quantified maps of the samples across large areas. Points in the grid were separated by 0.750 mm over an area of 25.5 x 8.25 mm, with the x-ray spot size an oval of 300 x 700 μ m. At each point a set spectra was generated at a pass energy of 160 eV, with a step size of 0.25 eV and 250 ms dwell time, with lenses in the hybrid mode and slot collimation to maximise S:N. Spectra were quantified using Kratos ESCApe, using Shirley backgrounds & the Kratos sensitivity factor library.

AFM

Atomic force microscopy (AFM) was performed using a JPK NanoWizard 3 instrument to produce nano-scale topographical measurements of the sample surface. Scans were performed at a rate of 0.7 Hz in alternating contact (AC) mode over a 2 x 2 µm area producing images at a resolution of 1024 x 1024 pixels. A gold-coated silicon supersharp cantilever (SHR150 provided by afm-probes.apexprobes.uk) was used to scan the sample surface at the resonant frequency of 150 kHz. Images were processed using Gwyddion software (Version 2.55) and the false colour maps presented here represent the topography of the sample surface. Topographical data is obtained from the processed images.



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Figure S1 JV Statistics of devices made with varying concentration of PTAA from 1mg ml⁻¹ to 3 mg ml⁻¹ with architecture glass-ITO-PTAA-MAPbI₃-PCBM-BCP-Ag via spin coating.



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Figure S2. Comparison of JV parameters of devices made on glass-ITO vs PET-ITO-PTAA(2.5mgm⁻¹l) vs PET-ITO-PTAA(5mgml⁻¹) via spin coating.

	S(PSS)	S(PEDOT)	N(ox)	N(NR ₃)	С	Na	In	Sn	0
ITO	N/A	N/A	N/A	0.17	19.1	N/A	29.1	2.83	48.7
ITO-PEDOT:PSS	5.1	1.4	1.6	0.15	66.4	0.90	1.75	0.07	22.9
ΙΤΟ-ΡΤΑΑ	N/A	N/A	N/A	2.4	51.2	N/A	17.5	2.0	26.9
ITO-PEDOT:PSS-PTAA	0.50	0.16	0.35	3.5	93.0	N/A	0.08	N/A	2.50

Table S3 Surface composition of the various layers by XPS at a single point for all three layers

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XPS Analysis PET-ITO-PEDOT:PSS films broadly give the expected elements for a PEDOT:PSS film: C, O & S (Table W). Carbon and oxygen are close to the expected theoretical At% for either PEDOT or PSS, but 6.5% sulfur is slightly lower than would be expected for a pure layer of PEDOT (11.1%) or PSS (8.3%). The presence of other species such as the presence of sodium (presumably as a PSS counter ion) and indium (from the underlying ITO) partly accounts for this. It should also be noted that, as this is a commercial formulation, other unknown compounds may be present to improve the processability of the formulation. For instance an "oxidised", peak denoted N(ox), is persistently observed at 401.9 eV. This binding energy is higher than would be expected for a typical organic compound, but would be consistent with, for instance, a quaternary amine.

The main component in the C(1s) is found at a low binding energy of 284.6 eV, consistent with the expected C=C in the PEDOT and PSS, again confirmed with the presence of the broad $\pi \rightarrow \pi^*$ feature at 291.2 eV. A shoulder is observed at 285.5 eV, attributed to carbons in close proximity to electron withdrawing groups such as the C-SO₃⁻. Finally, a large component is observed at 286.6 eV which would be typical of C-O bonds. The two sulfur components are also present, this time with a PSS:PEDOT ratio of 3.5:1 - this slight discrepancy with the 3:1 previously noted on the PTAA coating might indicate that either the composition is influenced by the PTAA processing or that the XPS is now sampling a layer of the PEDOT:PSS film closer to the top surface, which has a subtle composition variability to the bulk. Finally, stronger indium peaks are observed, which reflect the increased In seen in the maps in the main text.



Figure S4. "Typical" XPS spectra for the PEDOT:PSS films for N(1s), S(2p), C(1s) and In(3d). This particular location has a composition of 66.4% C, 22.85% O, 6.53%S, 1.75% N, 1.50% In, 0.90% Na & 0.07% Sn.

XPS Analysis PET-ITO-PTAA

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Note that this layer is particularly variable – refer also to Figure 2 in the main text. In the case of PTAA on ITO, a single N(1s) peak is observed at 400.1 eV. The C(1s) is also shifted to 284.9 eV. Whilst this would normally be considered consistent with the presence of C-C bonds, in this instance it is likely that this relatively thick, relatively poor conductive layer may be showing some surface charging. No S(2p) is expected in this film and the baseline spectra is included only for comparison to the other films. In(3d) attributable to the underlying ITO is observed at 445.0 eV.



Figure S5. "Typical" XPS spectra for the PTAA films for N(1s), S(2p), C(1s) and In(3d). This particular location has a composition of 94.8% C, 3.8% N, 0.99% O, and 0.33% In.

XPS Analysis PET-ITO-PEDOT:PSS-PTAA

As would be expected, the XPS spectra is dominated by the overlying PTAA. The nitrogen peak at 399.6 eV is consistent with the PTAA top layer, whilst the lower intensity peak centred at 401.4 eV represents an unknown, but more chemically oxidised species such as a quaternary amine, that is associated with the underlying PEDOT:PSS formulation. The C(1s) shows a strong main peak at 284.5 eV, consistent with the presence of a large contribution of aromatic carbon. This is further corroborated by the presence of the broad $\pi \rightarrow \pi^*$ feature at 291.1 eV. It should be noted that the expected presence of aliphatic carbon at 284.8 eV from the -CH3 groups in the polymer are not observed as a separate peak, due to the strong overlap with both the aromatic carbons and also with the distinct shoulder at 285.5 eV that is attributed to the tertiary-amine bound carbon atoms in the PTAA.^{1,2}

More surprisingly the two distinct 2p doublets associated with the underlying PEDOT:PSS are clearly visible. Although the atomic% is low, the expected two features from the underlying PEDOT:PSS are clearly observed. The highly oxidized PSS sulfur is observed at 167.9 eV, whilst the thiophene doublet appears at 164.0 eV.^{2,3} The ratio of PSS to PEDOT is consistently 3:1 across all locations. For large scale processing this is taken as a quality control measure – numerous methods for modifying the PEDOT:PSS have been developed ⁴, but one clear goal of large-scale processing is a consistent film over a large area.



Figure S6. "Typical" XPS spectra for the PEDOT:PSS-PTAA films for N(1s), S(2p), C(1s) and In(3d). This particular location has a composition of 93.0% C, 3.8% N, 2.5% O, 0.65% S and 0.08% In.

More surprising still is the presence of the indium 3d doublet that – in theory – should be buried beneath both PTAA and PEDOT:PSS. The In(3d5/2) peak is centred at 445.2 eV, which is consistent with ITO.⁵ Whilst the atomic% of this doublet is indeed low at 0.08 At%, and XPS detection limits are often described as being in the region of 0.1 - 1 At%, it should be noted that it is well known in the field that the 0.1 At% detection "limit" can vary considerably depending on the sample and analysis conditions. This is particularly true of the case of heavier elements in a light matrix as calculated by Shard et al.⁶ In the case of indium evenly distributed in a carbon matrix detection would be estimated to be 0.03 At%.





Figure S7. shows data used in the maps for PET-ITO-PEDOT:PSS-PTAA in the main text. In this case 210 spectra were stacked to consider any chemical – as opposed to compositional - variability on the samples. Whilst Intensity of peaks does vary as a function of location, chemical shifts are not observed.



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Figure S8 XPS Nitrogen atomic% map of R2R slot-die coated PET-ITO-PEDOT:PSS-PTAA,



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Figure S9 AFM images (10µmx10µm) of ITO-PET, as optimised R2R deposited PEDOT:PSS on ITO-PET, as optimised PTAA deposited on ITO-PET, as optimised PEDOT:PSS-PTAA deposited on ITO-PET.



Figure S10. Comparison of JV parameters of devices with varying wet film thickness of PEDOT:PSS buffer layer. PEDOT:PSS was R2R slot die and the rest of the layers were coated using spin coating.



Figure S11. Comparison of JV parameters of devices with varying wet film thickness of PTAA. In this experiment, PTAA was coated using the R2R slot die technique on top of a buffer layer that was also slot die coated. The remaining layers were coated using the spin coating method.



Figure S12. Comparison of JV forward and reverse scan parameters of the best batch with and without PEDOT:PSS buffer layer.

References:

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