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Author	Mikas Remeika, Luis K. Ono, Maki Maeda, Zhanhao Hu, Yabing Qi
journal or publication title	Organic Electronics
volume	54
page range	72-79
year	2017-12-19
Publisher	Elsevier B.V.
Rights	(C) 2017 Elsevier B.V.
Author's flag	author
URL	http://id.nii.ac.jp/1394/00000757/

doi: info:doi/10.1016/j.orgel.2017.12.027

High-Throughput Surface Preparation for Flexible Slot Die Coated Perovskite Solar Cells

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Abstract

To achieve industrially viable fabrication process for perovskite-based solar cells, every process step must be optimized for maximum throughput. We present a study of substituting laboratory-type UV-Ozone surface treatment with a high-throughput Corona treatment in a scalable perovskite solar cell fabrication process. It is observed that water contact angle measurements provide insufficient information to determine the necessary dose of Corona or UV-Ozone treatment, but the surface carbon signal measured by x-ray photoelectron spectroscopy accurately identifies when surface contamination has been completely removed. Furthermore, we observe highly accelerated de-contamination of ZnO surfaces by UV-Ozone treatment. The effect can be explained by photocatalytic O₂⁻ ion generation indicating that UV-Ozone treatment is also applicable in high-throughput processing.

1 Introduction

Perovskite solar cell power conversion efficiency has advanced at an unprecedented rate (up to 22.1% [1]) and is now competitive with many commercialized technologies such as CIGS (22.6% [1]) and CdTe (22.1% [1]). Solution processing is promising to lead to ultra-low-cost manufacturing, but commonly employed laboratory methods (e.g. spin coating) cannot be scaled to meet industrial production requirements. As a result, many laboratories are beginning to work with scalable fabrication methods such as slot-die coating ([2-8]) and ultrasonic spray coating ([9-15]) to ensure that advances in performance can be rapidly transferred to industrial production. Transitioning from spin-coating to scalable fabrication, researchers often discover that many aspects that could be considered negligible in small scale fabrication become important for scalable fabrication technologies.

Substrate surface preparation is a key aspect of fabrication that achieves high production yields. Contamination that is not eliminated during substrate preparation may affect every layer of the device. Furthermore, uniform surface condition over a large area is a prerequisite for uniform solution coating. Rapid processing is also a requirement because long process time impacts fabrication cost.

35 In this article we discuss an implementation of Corona treatment as a scalable substitute for UV-Ozone
36 treatment. UV-Ozone treatment is frequently employed in research laboratories to remove surface
37 contamination and increase surface energy of substrates (improve wettability) e.g., see [16, 17]. It is a
38 reliable technique, however, typical exposure times of 5-15 min make it poorly compatible with rapid
39 processing. Corona treatment is a rapid technique (sub-second treatment times) that is widely applied in
40 industry (e.g., for printing on plastic films) and is compatible with roll-to-roll processing. We present a
41 study of substituting UV-Ozone treatment with Corona treatment in a slot-die coating process for
42 perovskite solar cells and discuss some considerations that need to be taken into account when designing
43 a surface treatment process.

44 2 Materials and Methods

45 Device fabrication was accomplished as follows. Flexible PET film with pre-patterned ITO coating was
46 cleaned by high pressure air flow to remove surface particles, treated by adhesive roller (Teknek DCR
47 Hand Roller) to remove microscopic particles, and decontaminated with UV-Ozone (15 min) or Corona
48 (1000 W s/m^2) treatment. Electron selective layer was deposited by slot-die coating of ZnO nanoparticle
49 suspension (Nanograde N-10, 2.5% by weight in isopropanol (IPA), particle size 10-15 nm), with a substrate
50 speed of 0.6 cm/s, an ink pump rate 60 of $\mu\text{L/min}$, and the substrate temperature of 70°C . After coating,
51 the substrate was heated to 100°C (in air), annealed for 2 hours, then allowed to cool to room
52 temperature. PbI_2 precursor layer was deposited by slot-die coating solution of 0.47 mg/mL PbI_2 (Sigma
53 Aldrich) in DMSO (substrate speed 0.6 cm/s, temperature 70°C , ink pump rate $20 \mu\text{L/min}$. N_2 flow was
54 applied to accelerate evaporation of dimethyl sulfoxide during PbI_2 coating (see section 3.1). MAPbI_3 layer
55 was completed by slot-die application of the MAI ink (20 mg/mL in dehydrated IPA, substrate speed 0.6
56 cm/s, temperature 70°C , pump rate $70 \mu\text{L/min}$, repeated 3 times). Hole selective layer was deposited by
57 slot-die application of a P3HT-based ink (20mg P3HT, $7 \mu\text{L}$ Li-TFSI dopant (27 mg/mL Li-TFSI in Acetonitrile),
58 $3.5 \mu\text{L}$ 4-terp-butylpyridine, 1 mL O-Dichlorobenzene, prepared with dehydrated solvents in N_2 glove box),
59 substrate speed 0.6 cm/s, temperature 70°C , pump rate $45 \mu\text{L/min}$, repeated 3 times. Device area of
60 1cm^2 was defined by thermal evaporation of an Au electrode (80 nm). In all cases the slot die applicator
61 width was 12 mm. Unless otherwise specified, solvents were regular non-dehydrated grade. Reagents
62 were used as received, without further purification.

63 UV-Ozone treatment was performed for a specified length of time by a table top UV-Ozone treatment
64 system capable of treating rigid or flexible substrates (Jelight 42A-100). Corona treatment was performed
65 by a Vetaphone CP-Lab corona treatment system designed to process flexible substrates. Corona
66 treatment system was operated at substrate speed of between 4 and 10 m/s.

67 Electrical characterization of devices was performed by ORIEL Sol1A solar simulator and Keithley 2420
68 source-measure unit, with dwell time of 100 ms at each measured point. Cross-sectional images were
69 obtained by FIB milling and SEM imaging using FEI Helios G3 dual beam system. Optical microscope images
70 were acquired by a Leica DM4000 B microscope.

71 The surface electronic properties of ZnO were characterized by XPS (Kratos AXIS ULTRA HAS,
72 monochromated $\text{Al-K}\alpha = 1486.6 \text{ eV}$) in order to observe effect of UV-ozone and Corona treatments on the
73 surface chemical compositions. The binding energy (BE) was calibrated by measuring the Fermi edge ($E_F =$
74 0 eV) and $\text{Au-4f}_{7/2}$ (84.0 eV) on a clean Au surface. Great care was taken in order to mitigate X-ray exposure
75 time when characterizing ZnO samples. X-ray induced sample damage was monitored by taking five

76 consecutive scans and comparing these spectra. Acquisition time for each scan varied from 20 to 70 s
 77 depending on the core level regions. The five scans were averaged to a single spectrum if significant
 78 change was not observed. XPS intensities for each chemical component was normalized with respect to
 79 the Zn 2p_{3/2} signal height at BE of 1022.5 eV.

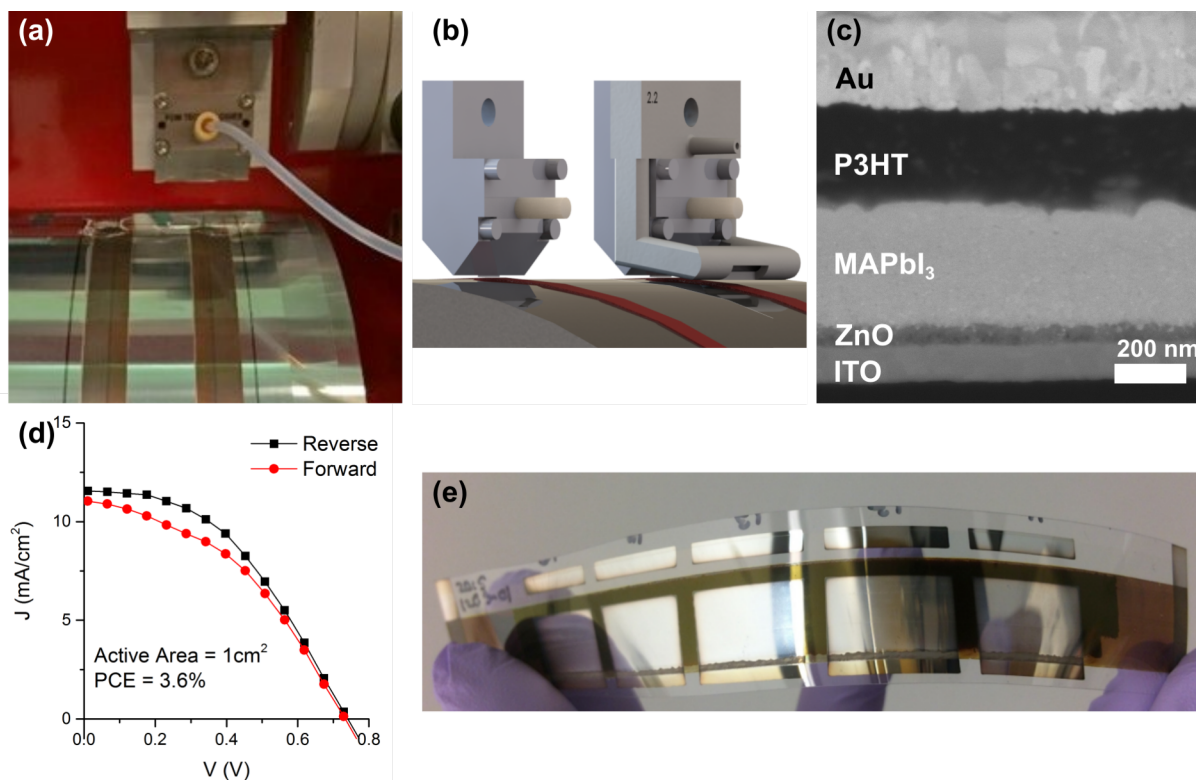


Figure 1. (a) Application of perovskite absorber by slot die coating. Slot die head is shown elevated immediately after coating MAI solution over Pbl₂. Red stripes are perovskite strips formed immediately after coating Pbl₂ by MAI. (b) Drawing of the slot die head with (right) and without (left) the air flow nozzle used to accelerate drying on Pbl₂ immediately after slot die coating (not shown in (a)). (c) SEM cross section image of the slot-die coated perovskite solar cell on a flexible PET substrate. (d) IV characteristic of a top performing device under AM1.5 illumination. Forward and reverse voltage sweeps are shown to demonstrate minimal hysteresis. (e) A strip of flexible solar cells fabricated by slot-die coating. Each device has active area of 1 cm².

80

81 3 Results and Discussion

82 3.1 Device Fabrication

83 To advance scalable fabrication technology for solution processed perovskite solar cells, a table-top slot-
 84 die coating system was used to develop a roll-to-roll compatible coating process. Slot-die coating is
 85 commonly employed in industry for high-throughput coating, and in recent years laboratory sized
 86 machines have become available. Small scale slot-die coating tools allow development of coating
 87 processes with only a small investment, and permit a rapid transfer of technology from laboratory to large
 88 scale production. Several groups have demonstrated slot-die coating of functional layers for perovskite
 89 solar cell fabrication [2-8].

90 The proof-of-concept process was designed to employ low cost materials, in particular substituting P3HT
 91 for a more conventional spiro-MEOTAD, due to lower cost and an established record of reliable large area

92 coating. We implemented a device structure of polyethylene terephthalate (PET) \ Indium Tin Oxide (ITO)
93 \nanoparticle (np-)ZnO\ MAPbI₃ \ doped poly(3-hexylthiophene-2,5-diyl) (P3HT) \ Au with np-ZnO,
94 MAPbI₃, and P3HT layers applied by slot-die coating (details of device fabrication can be found in Section
95 2). UV Ozone / Corona treatment was applied to ITO surface before coating ZnO nanoparticle ink, and to
96 ZnO surface after annealing (before coating PbI₂ precursor to MAPbI₃).

97 Slot die coating was accomplished using a Mini Roll Coater by FOM technologies. Figure 1a shows the roll
98 coating tool immediately after coating MAI ink over PbI₂ precursor. For the purpose of coating the PbI₂
99 precursor layer the system was modified to add a gas quench system, similar to what was implemented
100 by Hwang et al[3]. Solvent evaporation rate dramatically affects the texture of solution coated PbI₂ films
101 and we found that uniformly translucent films could be achieved if the slot-die coating head was followed
102 immediately by nitrogen nozzle that uniformly applied a strong flow of nitrogen over the wet PbI₂ film. A
103 3D rendering of the nozzle design mounted on the slot-die head is shown in Figure 1b. The nozzle was
104 fabricated by 3D printing and is specifically designed to apply a uniform laminar flow of gas onto the wet
105 film, while preventing flow of gas toward the slot die head which could disturb application of liquid ink.

106 The cross-sectional SEM image of the fabricated device is shown in Figure 1c. Maximum power conversion
107 efficiency achieved by such a device is 3.6 % with negligible hysteresis (Figure 1d). Several complete
108 devices are shown in the Figure 1e. The main goal of this work was to study the implementation of high-
109 throughput Corona treatment to perovskite solar cell fabrication; therefore, optimization of slot-die
110 coated device performance will be addressed in future work. The complete devices are presented here as
111 a proof concept, to demonstrate that processing conditions were appropriate for device fabrication.

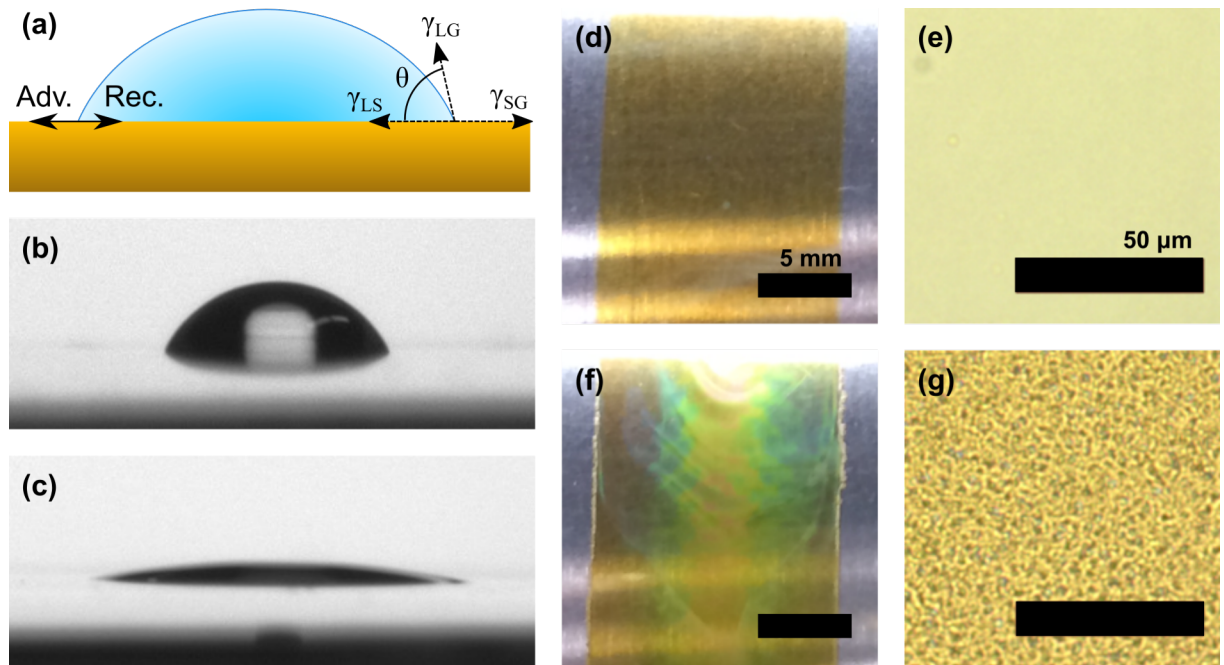


Figure 2 (a) Schematic of a water droplet on a solid surface. γ_{SL} , γ_{LG} , and γ_{SG} are solid-liquid, liquid-gas, and solid gas surface/interface tension forces respectively. When the three forces balance, contact angle of θ is achieved. Left side of the drop indicates directions of advancing and receding liquid edge (see Appendix A). (b) water droplet profile photo on an untreated ITO surface. (c) Water droplet profile photo on a ITO substrate after 15 min UV-Ozone treatment. (d) Visually smooth PbI_2 texture obtained by coating ZnO treated with UV-Ozone. (e) Transmission optical microscope image of smooth PbI_2 obtained by coating UV-Ozone treated ZnO. (f) Visually rough texture of PbI_2 obtained by coating insufficiently Corona treated ZnO, scale bar is the same as (d). (g) Transmission optical microscope image of PbI_2 obtained by coating insufficiently Corona-treated PbI_2 , scale bar is the same as (e).

112

113 3.2 Surface Treatment

114 Three types of surface treatments by reactive oxygen are common in research laboratories: UV-Ozone,
 115 Corona, and Oxygen Plasma. See Appendix B for a detailed discussion. While all three treatments achieve
 116 surface decontamination by exposure to reactive oxygen species, methods of atomic or ionic oxygen
 117 generation differ. These differences may lead to unexpected results if the decontamination method is
 118 changed. Effects of UV-Ozone treatment and Corona treatments were compared to determine how a high-
 119 throughput Corona treatment could be substituted for UV-Ozone treatment. Due to inherently high cost
 120 and slow processing, oxygen plasma was not tested.

121 To quantify effect of UV-Ozone and Corona treatment on surface condition we measured the contact
 122 angle of a water droplet placed on the surface. This method is low-cost and non-destructive (see Appendix
 123 A). Figure 2a shows schematic of a water droplet and the measured contact angle. Figure 2b,c shows
 124 profile photos of water droplet before (after) 15 min UV-Ozone treatment on an ITO substrate. Initial
 125 testing indicated that 1000 Ws/m^2 dose of Corona treatment of an ITO film achieved water contact angle
 126 equivalent to 15 min UV-Ozone treatment.

127 When 1000 Ws/m^2 Corona treatment was substituted for UV-Ozone treatment of ITO film (before ZnO
 128 coating) no effect on film quality of device performance was observed and it was concluded that Corona
 129 treatment was a good substitute for UV-Ozone treatment.

130 Assuming the treatment rate was the same for ZnO as for the ITO surface, PbI₂ coating was tested on ZnO
 131 surfaces treated with 15 min UV-Ozone and 1000 Ws/m² Corona treatment. PbI₂ coated on ZnO films
 132 treated with UV-Ozone showed uniformly translucent texture, see Figure 2d,e. Unexpectedly, it was
 133 observed that ZnO films cleaned with Corona treatment frequently resulted in non-uniformly hazy texture
 134 of PbI₂ films, see Figure 2f,g.

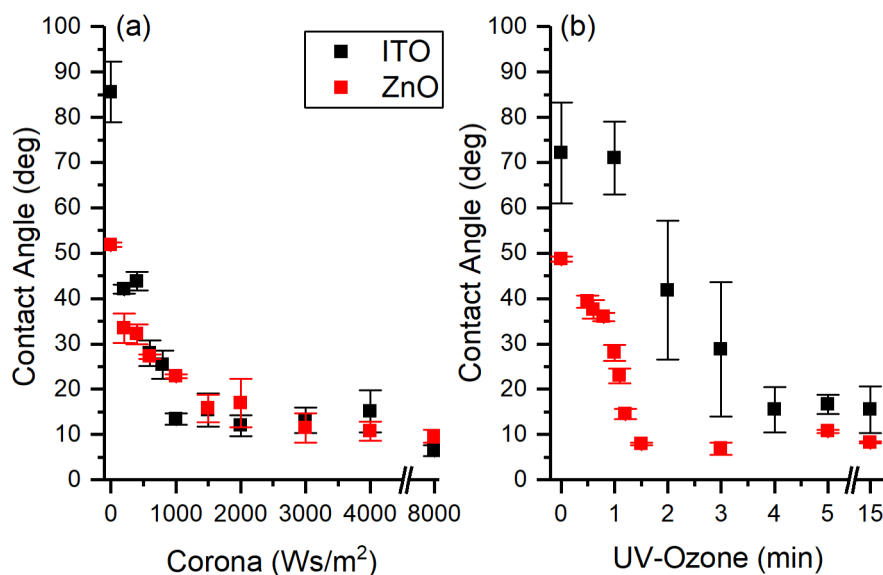


Figure 3.(a) Water contact angle dependence on corona treatment dose for ZnO (red squares) and ITO (black squares) surfaces. (b) Water contact angle dependence on UV-Ozone treatment time for ZnO (red squares) and ITO (black squares) surfaces. Error bars indicate standard deviation of three droplets measured for each treatment condition.

135
 136 A detailed investigation of water contact angle dependence on UV-Ozone and Corona treatment dose was
 137 conducted. Figure 3a and b show the dependence of water drop contact angle on ITO and ZnO surfaces
 138 as a function of Corona and UV-Ozone treatment, respectively. The result indicated that water contact
 139 angle on ITO and ZnO depends very similarly on Corona treatment dose, however that is not true for UV-
 140 Ozone treatment. As seen in Figure 3b, UV-Ozone treatment decreases the water contact angle on ZnO
 141 dramatically faster than on an ITO surface. Although the water contact angle on a ZnO surface after 1000
 142 Ws/m² Corona treatment is close to the contact angle achieved by 15 min UV-Ozone treatment, the
 143 texture of PbI₂ coated over Corona treated ZnO showed significant differences. UV-Ozone treatment
 144 achieves saturation (minimum measurable contact angle) after just 2 minutes on ZnO and around 1500
 145 Ws/m² for Corona treatment. This observation suggests that some contamination may remain on the
 146 surface that cannot be detected by water contact angle measurements, but is removed by additional
 147 oxygen treatment.

148 To characterize surface contamination state, an XPS measurement was employed to quantitatively
 149 measure presence of carbon compounds on the sample surface. Figure 4 shows C 1s and O 1s XPS signals
 150 (normalized with respect to the Zn 2p_{3/2} peak height at the binding energy of 1022.5 eV) for ZnO surfaces
 151 treated with UV-Ozone and Corona. The raw XPS spectra were fitted with Gaussian-Lorentzian function in
 152 CASA XPS 2.3.16 software. Curve-fittings of XPS C 1s and O 1s core-level spectra were performed following
 153 procedure described in previous publication [16]. In Zn 2p core-level region (not shown), only a single

154 oxidation state with full width at half maximum (FWHM) of 1.7 eV in Zn 2p_{3/2} peak was measured and
 155 most likely associated with ZnO, ZnO_x, ZnOH, and/or C-Zn-O in agreement with previous reports[16, 18-
 156 21]. The C 1s core-level region exhibited three main chemical states at 285.5 eV, 287.3 eV and 289.5 eV
 157 (Figure 4a and c, marked 1,2,3 respectively)[16, 18-21]. As described in previous works, [16, 18-20] precise
 158 assignments of these carbon peaks are complex and an independent investigation will be required to
 159 correctly assign the chemical states in C 1s. Following literature, we tentatively assign the peak at 285.5
 160 eV to adventitious carbon present at surface and bulk, 287.3 eV peak to surface contaminations related
 161 to O-C-O complexes (e.g. storage in air) [16, 18-20], and 289.5 eV peak to incorporated oxygen atoms at
 162 the interstitial sites of ZnO forming O-C-Zn complexes [16, 18] and/or shake-up line [22-25].

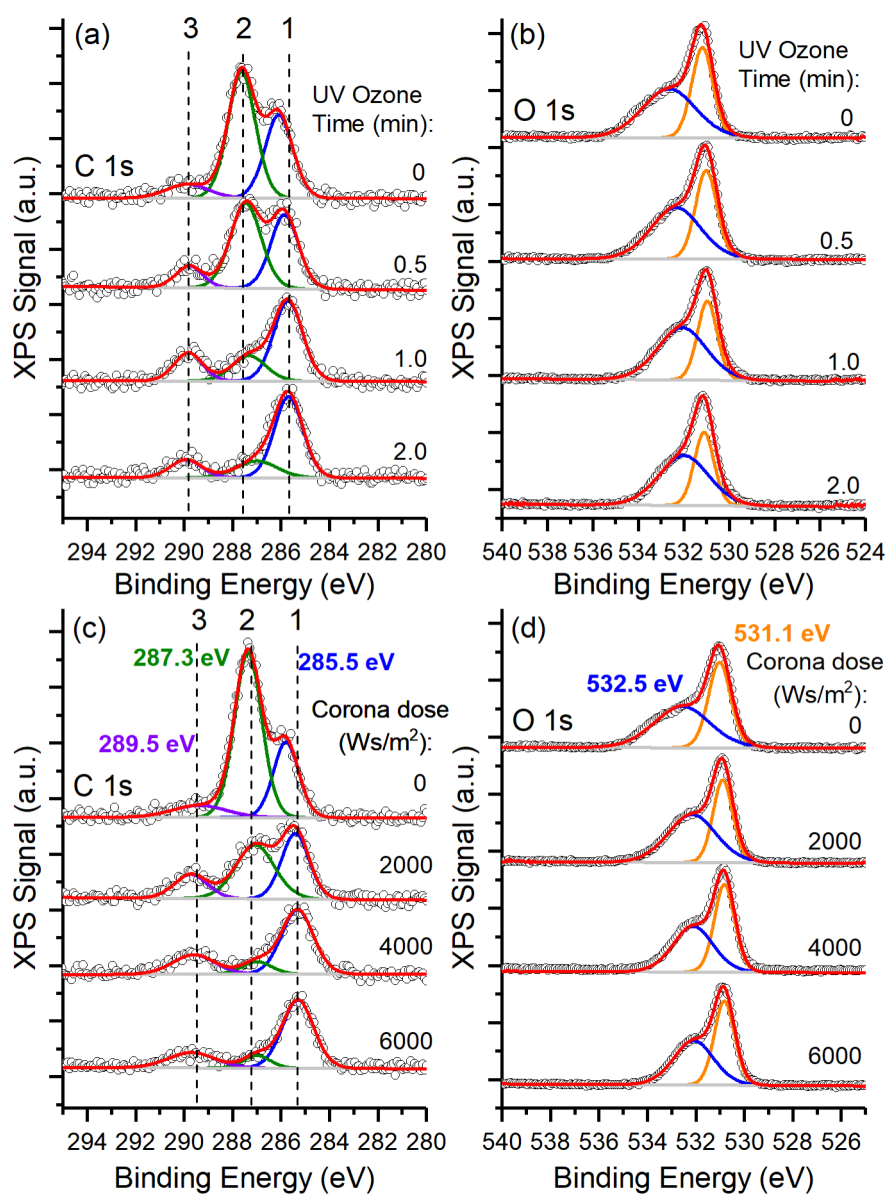


Figure 4 XPS signal of (a) C 1s and (b) O 1s after varying UV-Ozone treatment. XPS signal of (c) C 1s and (d) O 1s after varying Corona treatment. All XPS data were normalized to Zn 2p peak at 1022.5 eV. Plots in (a), (b), (c), and (d) are offset for clarity.

164 In this study, we focused on the systematic trend changes in the C 1s features that were correlated with
165 slot-die coated PbI_2 film quality. It is observed that both types of treatment result in rapid decrease of C
166 1s signal at the binding energy of 287.3 eV (peak 2 in Figure 4a and c). Figure 5 summarizes dependence
167 of C 1s peaks on UV Ozone and Corona treatment. It is observed that in agreement with water contact
168 angle measurement, the 287.3 eV signal reaches a minimum value for UV-Ozone treatment after 2
169 minutes. For Corona treatment, after a dose of 2000 Ws/m^2 a substantial signal is still remaining at the
170 binding energy of 287.3 eV. 4000 Ws/m^2 dose reaches the minimum C 1s signal value at the binding energy
171 of 287.3 eV. In contrast, water contact angle measurements show no changes after Corona dose of 1500
172 Ws/m^2 , see Figure 3a. In addition, it was considered that oxidation of the surface could lead to increased
173 surface energy. The O 1s XPS signal is shown in Figure 4b and d. Similar to the C 1s region, XPS
174 deconvolution in O 1s region is complex and further systematic studies will be required to assign correctly
175 the chemical compounds (e.g. corroborated by FT-IR) present in our ZnO films. Comparing with literature
176 reports[16, 18-20], the O 1s region is often deconvoluted in (i) stoichiometric ZnO lattice ($\sim 531.1 \text{ eV}$) and
177 (ii) defective ZnO_x and/or hydroxyl complex of ZnOH (532.5 eV). However, because carbon-related
178 contaminants are expected to contain oxygen atoms, our O 1s region is also expected to include these
179 contaminants making the deconvolution of O 1s challenging. Because the O 1s peaks affected only slightly
180 by Corona or UV-Ozone treatment, we conclude that surface energy increase is primarily due to organic
181 (carbon containing) impurity removal.

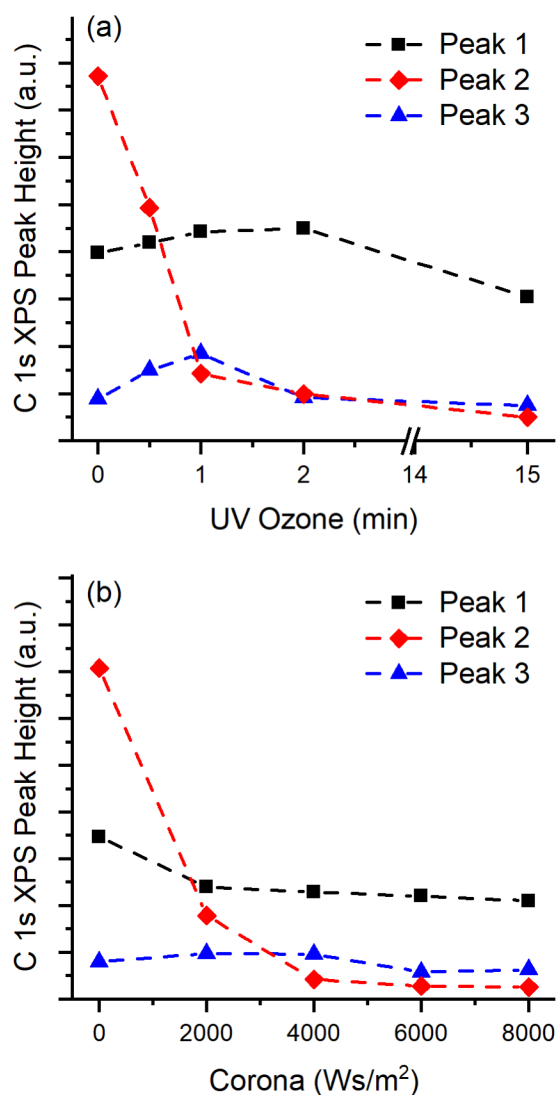


Figure 5 XPS signal of C 1s varying with (a) UV ozone and (b) Corona treatments. Peak positions of 1, 2, and 3 are marked in Figure 4.

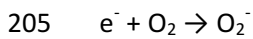
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183

184 Based on the observation that C 1s 287.3 eV XPS signal was undetectable after 4000 Ws/m² dose of Corona
 185 treatment, Pbl₂ coating process was tested with this Corona treatment dose. With the Corona treatment
 186 done increased to 4000 Ws/m² visually observed Pbl₂ film quality became equivalent to what was
 187 observed for UV-Ozone treatment (Figure 2d-g). It was concluded that vanishing of the C 1s 287.3 XPS
 188 signal was an indication of sufficient surface decontamination, and Corona treatment was good substitute
 189 for UV-Ozone treatment. Due to many factors affecting the quality of solution processed devices
 190 fabricated in ambient air, it is not straightforward to quantify the effect of a surface treatment on device
 191 performance. To confirm our conclusion that increased Corona treatment dose improved film uniformity
 192 and reproducibility we analyzed performance data of batches fabricated before and after it was
 193 understood that that Pbl₂ texture was affected by insufficient Corona treatment dose. Figure 6 shows

194 averaged PCE values for a series of device batches fabricated over a period of 3 months. A substantial
195 increase in mean PCE and a reduction of standard deviation of device performance is observed after
196 increased Corona treatment dose is implemented.

197 To understand the reason why a UV-Ozone, but not Corona treatment shows improved effectiveness on
198 ZnO surface, we can consider the differences between two processes. Both processes generate atomic
199 oxygen, but UV-Ozone also includes exposure to high energy UV radiation, while Corona does not. Both
200 ITO and ZnO are high band-gap (ITO approx. 4 eV, ZnO approx. 3.3 eV) n-type semiconductors, and both
201 are capable of absorbing the UV-light of UV-Ozone treatment (245 nm ~ 4.88 eV, 185 nm ~ 6.70 eV).
202 However, ZnO is also known to be an efficient photocatalyst, with applications to pollutant decomposition
203 [26]. An example of a photo-catalyzed reaction that could take place in presence of air and ZnO is
204 reduction of molecular oxygen:



206 Superoxide (O_2^-) is a very reactive species that would be generated on the ZnO surface and accelerate
207 decomposition of organic contaminants. Possible observation of photocatalytically assisted UV-Ozone
208 decontamination suggests that a high-throughput UV-Ozone process could also be developed for selected
209 surfaces. Furthermore, it is possible to develop a selective treatment process that would affect only
210 photocatalytically active surfaces with minimal effect on other areas. This could be advantageous when
211 the sample includes organic materials that could be damaged by extended oxygen treatment.

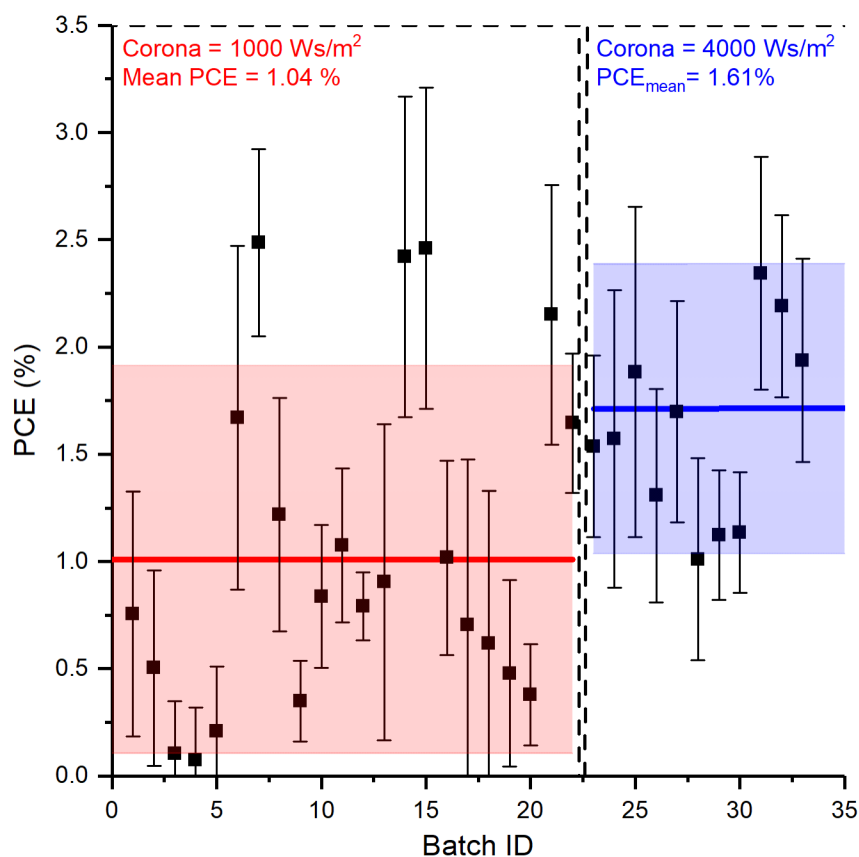


Figure 6. Performance data of slot-die coated samples fabricated over a time period of three months. Each data point represents a batch of 15 devices, of active area 1 cm^2 , structure is illustrated in Figure 1c and e. Error bars are standard deviations. PCE is calculated by averaging forward and reverse IV measurements. Red solid line indicates mean PCE for samples treated with Corona dose based on ITO water contact angle measurement (1000 Ws/m^2). Blue solid line indicates mean PCE for samples treated with Corona dose based on XPS surface carbon measurement on ZnO surface (4000 Ws/m^2). Filled area indicates standard deviation. Batches are presented in chronological order of fabrication.

212

213 4 Conclusions

214 Key result of this study is that while water contact angle is a good guide to a degree of de-contamination
 215 achieved by different methods, trace contamination unresolvable through water contact angle may
 216 strongly affect uniformity of solution coated perovskite precursors. XPS carbon atomic density
 217 measurement provides a quantitative tool with the right sensitivity to identify full de-contamination of
 218 the surface. Water contact angle measurement followed by XPS measurement close to the optimal dose,
 219 is a cost-effective technique of determining correct oxygen treatment dose.

220 XPS measurement of carbon and oxygen density on ZnO surface suggests that the primary effect of Corona
 221 and UV-Ozone treatments is to remove carbon-containing contaminants rather than oxidize the surface.
 222 This is likely because ZnO is already an oxide, but may not be true for other types of surfaces.

223 We have successfully demonstrated that UV-ozone treatment could be substituted with high-throughput
 224 Corona treatment in a slot-die coating process for a perovskite solar cell. Equivalent PbI_2 film quality was

225 achieved with treatment time (for a 10 x 10 cm substrate) reduced from 15 min (UV-Ozone) to 0.1 s
226 (Corona).

227 It is observed that decontamination of ZnO surface by UV-Ozone is greatly accelerated, compared to ITO
228 surface. This effect is not observed for Corona treatment. A possible explanation for this effect is
229 photocatalytic production of O_2^- (superoxide ion) on the surface of ZnO due to UV light exposure. Presence
230 of superoxide ion would accelerate decomposition of surface adsorbed organic species. Rapid
231 decontamination of ZnO by UV-Ozone suggests that even UV-Ozone may be useful in high-throughput
232 production. In particular, if delicate polymer substrates are employed, UV-Ozone could be employed to
233 selectively treat ZnO coated areas, with reduced risk of damage to the polymer substrate.

234 5 Acknowledgements

235 This work was supported by funding from the Energy Materials and Surface Sciences Unit of the Okinawa
236 Institute of Science and Technology Graduate University, the OIST R&D Cluster Research Program, and the
237 OIST Proof of Concept (POC) Program.

238

Appendix A. Surface energy

The surface treatments discussed in this article are primarily aimed at de-contamination of surfaces and increasing the surface energy, therefore the concept of surface energy is briefly discussed. Surface energy is defined as the energy required to change the surface area of an object by a unit of area. The concept originates from the fact that surface atoms are not uniformly surrounded by identical atoms (unlike the atoms inside the solid or liquid) and therefore exist in a higher energy state. An alternative term “surface tension” is also frequently used to refer to surface energy of liquids. The terms refer to the same quantity and the common surface tension units of dyn/cm are equivalent to surface energy unit of mJ/cm^2 . For a liquid, surface energy can be determined directly by measuring energy required to stretch a fixed liquid volume, therefore increasing its surface area. For a solid, deformation would involve many other energy-consuming processes, therefore literal implementation of the definition is not practical.

Many methods of measuring solid surface energy exist, but two simple methods are most common in non-specialized laboratory settings: water contact angle and dyne liquids [27]. Dyne liquids are special mixtures of known surface tension available in increments of 10 dyn/cm. Drawing a line on the surface of a solid by a specified dyne liquid pen will result in a line that is either continuous or breaks into beads. A continuous line indicates that solid has higher surface energy than the dyne liquid and vice versa.

The water contact angle method means placing a small drop of water on the surface and using a camera to photograph the water drop profile. The contact angle of the water to the solid surface will depend on the surface energy of the solid. In a highly idealized case of a pure water droplet on a perfectly clean solid surface, contact angle can be related to surface energy via Young equation:

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos \theta$$

Where γ_{SG} is surface energy of the solid-gas interface, γ_{SL} is surface energy of the solid-liquid interface, and γ_{LG} is surface energy of the liquid-gas interface (see Figure 2a). Differences between the three surface energies act like forces to displace the edge of the liquid drop and equilibrium is achieved when all three

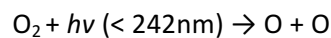
exactly cancel. In a practical measurement, droplet edge will generally be pinned to some extent, and the measured contact angle will depend on whether the liquid edge was advancing or receding before stabilizing (see Figure 2a). The true equilibrium angle is between advancing and receding values, but cannot be determined by any simple method. In practice, however, to compare surface energies of surfaces, identical droplet placement will ensure that contact angle difference will reflect difference in surface energy.

Equilibrium contact angle between liquid ink and the substrate is a crucial parameter that determines the uniformity of coating. A high contact angle will result in dewetting of ink rather than uniform coverage of the substrate. Even when complete coverage is achieved, a high contact angle may lead to slow equilibration of ink into a flat wet film. Slow equilibration may result in precipitation of ink solids before a flat wet film is achieved, which is highly detrimental to coating uniformity. Therefore, various surface treatments are applied to maximize surface energy and ensure rapid wet film equilibration. It is worth noting that while contact angle measurements are typically performed with water droplets, the obtained estimate of surface energy is applicable to coating with any solvent. Most organic solvents have low surface tension (< 40 dyn/cm) while water has high surface tension (74 dyn/cm) resulting in a higher contact angle and higher precision of measurement. However, even with a low surface tension solvent, maximizing substrate surface energy is desirable for rapid equilibration of ink coating.

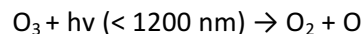
Appendix B. Types of surface treatment

Three dry surface cleaning methods are popular in typical semiconductor process laboratories: UV-Ozone, Oxygen plasma, and Corona discharge. All three methods accomplish the goal of removing contaminants from the surface and partially oxidizing the surface. Both de-contamination and oxidation act to increase surface energy and are not distinguishable by liquid contact angle measurements. However, formation of oxide layer could impact charge carrier transport through the interface between functional layers and affect device performance.

UV-Ozone treatment is accomplished by placing the sample in an enclosed chamber illuminated by a UV light. A typical apparatus uses the mercury discharge light which emits UV light at wavelengths of 185 nm and 254 nm. 185nm light is absorbed by oxygen present in air (while 254 nm is not) and causes formation of atomic oxygen and ozone [28]:



Where M is any neutral molecule that is necessary to conserve momentum. Ozone strongly absorbs UV light (including the 254 nm light) and decomposes via reaction



The highly reactive atomic oxygen will oxidize surface molecules of the sample and adsorbed contaminants. Organic molecules that decompose into volatile species under oxidation will leave the surface, and the sample is effectively cleaned. Oxygen will also react with sample surface to form oxide and hydroxide groups which have higher surface energy, increasing the wettability of the surface.

UV light that is not absorbed by air may be absorbed by the surface and also cause decomposition of surface contaminants. It was observed in [17] that exposure to either UV light (wavelength > 242 nm, with

insufficient photon energy to generate ozone) or ozone caused the surface cleaning to occur at a slow rate, whereas exposure to both resulted in contamination removal about 100 times faster. Observation was interpreted to mean that exposure to UV light greatly increases reactivity of surface contaminants and atomic oxygen.

UV-Ozone cleaning is popular due to its simple operation and low maintenance. The rate of treatment depends on the distance to the UV lamp, but sample height variations on the order of centimeters can be accommodated in a typical laboratory setup.

Corona discharge treatment is accomplished by passing a sample surface close to an arc discharge between two high-voltage electrodes in air. Alternating high voltage between the electrodes accelerates naturally occurring free charges, causing high energy collisions and further ionization of the air. The discharge results in a high concentration of atomic oxygen which oxidizes contaminants on the surface. Oxidized organic molecules that form volatile species are removed. Surface of the sample is also oxidized introducing oxide and hydroxide groups, which have high surface energy and increase wettability of the surface [29]. Ozone is also generated in the process, but in absence of UV-illumination it does not play a significant role in the surface treatment. Instead, Ozone generation needs to be considered from the safety perspective to ensure that this toxic gas is channeled to appropriate exhaust.

The absence of UV illumination in the process means that the treatment is confined strictly to the surface of the sample and there is no risk of UV radiation penetrating and damaging the substrate. Generally Corona treatment is applied to flat surfaces or continuous films, because a uniform treatment requires uniform distance (with sub-millimeter accuracy) between the sample and the electrode. Variations of Corona treatment tools exist that channel the plasma using a flow of air making it possible to treat non-flat surfaces. However, the majority of the plasma is still confined to the vicinity of electrodes making this process much less energy efficient [29].

Oxygen plasma treatment is accomplished by placing a sample in a sealed chamber filled with oxygen at a low pressure between 1000 mTorr and 10 mTorr. An alternating electric field (frequency in the KHz – MHz range) is applied to accelerate naturally occurring ions, which causes further ionization, until a large fraction of the gas becomes ionized. Resulting atmosphere of ionized atomic oxygen is extremely reactive and will rapidly oxidize any un-oxidized species. Organic and other carbon-containing compounds will typically form volatile species and be removed from the chamber by the vacuum system.

The plasma treatment is the most powerful of the three methods described in this work. It is the only method that is capable of rapidly removing bulk quantities of organic materials. For that reason it is not suitable for treating substrates containing functional organic materials deposited intentionally. Any organic components exposed to the plasma will be damaged or completely removed.

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