Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

Rapid Scalable Fabrication of Roll-to-Roll Slot-die Coated Flexible Perovskite Solar Cells Using Intense Pulse Light Annealing

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a) Optimization of roll-to-roll slot-die coating of SnO_2 layer:

The SnO_2 precursor solution was prepared in two different methods to adjust the wettability and evaporation of the inks. The first method, the commercial SnO_2 solution is diluted with DI water (1:3 vol. ratio) having a 12 µl of Triton X 100 surfactant. The surfactant improved the film wetting but due to the slow evaporation produced films with uneven drying patterns. In the second method, the commercial SnO_2 was diluted with DI water and isopropanol (IPA) in different volume ratios of 3:1, 1:1 and 1:3. The addition of IPA improves the wettability and evaporation of the inks. However, as the addition of IPA increased, noticed a turbidity in the SnO_2 solution, and the viscosity could overcome the capability of the slot die deposition. This increase in viscosity is also related to the amount of the IPA added to the ink and their corresponding images are shown in Figure S1. SnO_2 deposition was carried out on a PET substrate by adjusting the solution flow rates in the range of 0.5 to 2 ml/min and different web speeds from 0.5 to 2 m/min (see Table S1), where the thickness varies linearly with the flow rate and inversely with the web speed. The optical images of as deposited SnO_2 films are also shown in Figure S2. To overcome the issues with the turbidity, anhydrous ethanol was introduced in lieu of IPA. After optimization on PET substrates, the roll-to-roll deposition of SnO_2 was carried out on ITO/PET substrates using the same method described above. 12 µL of Triton X 100 surfactant was added to address the difference in surface energy of ITO and PET. The corresponding optical and SEM images of as deposited SnO_2 films are presented in Figure S3, exhibiting a uniform deposition without any voids across the web.

Table S1

Deposition of SnO_2 at a constant web speed of 1.5 m/min		Deposition of SnO_2 at a constant flow rate of 1.8 ml/min	
Flow rate (ml/min)	**Average Thickness (nm)**	**Web speed (M/min)**	**Average Thickness (nm)**
1.2	45	1.5	100
1.5	54	1.8	85
1.6	68	2.0	72
1.8	84	2.5	58
2.0	125	3.0	50

Table S1: The variation in the thickness of roll-to-roll slot-die coated SnO_2 layer by changing different flow rates and web speeds.

Figure S1

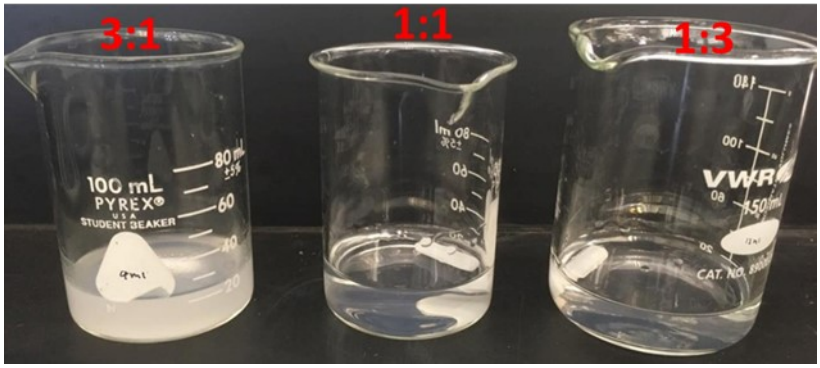


Figure S1: Optical images of dilution of commercial SnO_2 with DI water and Isopropanol in different volume ratios of 3:1, 1:1, and 1:3.

Figure S2

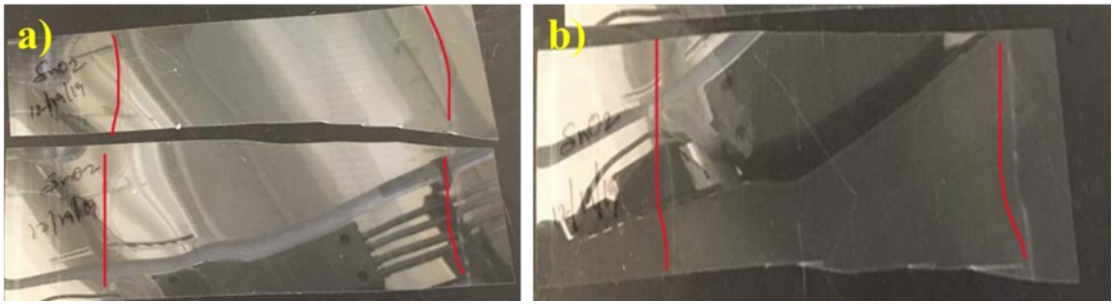


Figure S2: Optical images of roll-to-roll slot-die coated SnO_2 films with a web speed of 1.5 m/min, and flow rate of 2 ml/min (red lines are the edges of SnO_2 film).

Figure S3

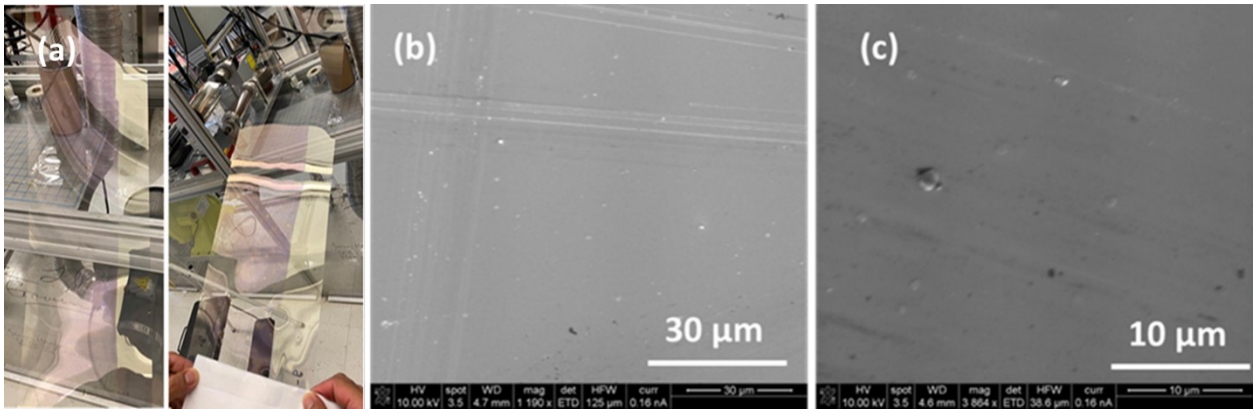


Figure S3: Optical and SEM images of roll-to-roll slot-die coated SnO_2 films.

b) Effect of concentration of perovskite precursor inks and solvent system:

The perovskite layer was initially deposited using higher concentrations (1 M) of perovskite precursor inks dispersed in DMF and DMSO (0.7:0.3 vol. ratio) solvents. The resulting films exhibited non-uniformity and large gaps/pinholes as shown in Figure S4. The obviously large gaps in the coating are attributed to poor wetting between the perovskite ink and the SnO_2 film. It is also evident that the formation of a highly discontinuous film with isolated islands defined by a capillary boundary as shown by the SEM images in Figure S5. It is attributed to the incomplete drying of wet perovskite film under the air-knife pass, which is a direct consequence of the precursor ink consisting of high boiling points solvents. Reducing the concentration to a 0.5M solution resulted in a pale colored perovskite film having high volume of small size pinholes as shown in Figure S6. It was found that a formation of long needle like dendritic structures occurred as shown in Figure S7, which would be an indication of an adduct formed with the DMSO. With the proposed fast drying and annealing techniques, this solvent proved difficult to integrate into a large area deposition and can be attributed to the poor wetting and adduct formation.

Crystallization of roll-to-roll slot-die coated perovskite film is strongly influenced by the precursor solvents, drying and annealing conditions. The morphology of slot-die coated perovskite films having solvents of DMF and DMSO exhibited an incomplete conversion of perovskite crystals and appeared as dendritic needle like structures as shown in Figure S7, and their corresponding optical images of perovskite films are also shown in Figure S6. The formation of needle like structures are ascribed to an incomplete solvent evaporation and presence of complex

adduct MAI.PbI_2.χDMSO in solution which serves as heterogeneous nucleation sites which results into formation of bulk structures by Van der Waals bonding. Hence, the use of regular solvents like DMF and DMSO were eliminated and the low boiling point solvents of ACN and 2-MeOH were used. Thus, the combination of volatile coordinating solvents (ACN:2-MeOH in 3:2 vol. ratio) favors a rapid drying with the film immediately developing into a black color perovskite phase and the corresponding optical image is shown in Figure S8a. The quick solvent evaporation forms smooth, uniform perovskite films, however, they exhibited poor contact to the substrate and small grain sizes as shown Figure S8b. To improve the adhesion and perovskite crystallinity, trace amounts of LP surfactant and DMSO (20 mol%) were added.

Figure S4

Figure S4: Optical images of roll-to-roll deposited perovskite films from the higher concentrations (1M) perovskite precursor ink consists of DMF and DMSO solvents.

Figure S5

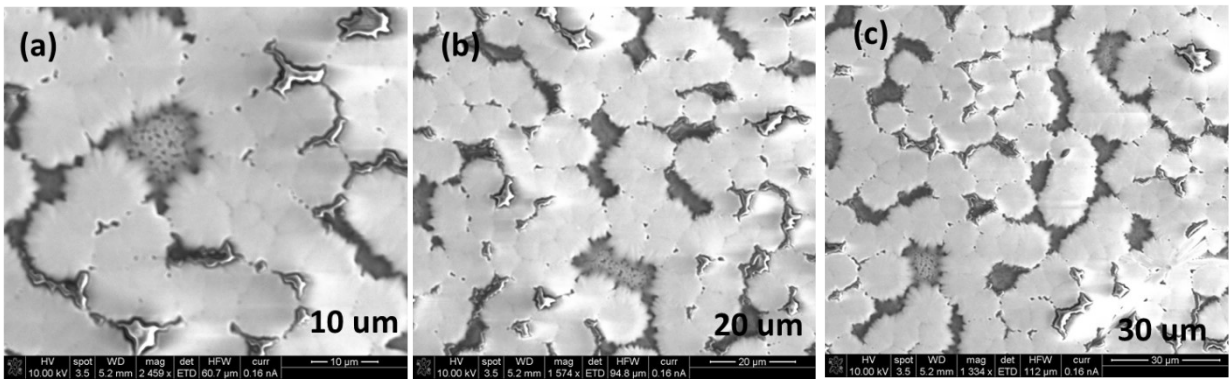


Figure S5: SEM images of roll-to-roll deposited perovskite films from the higher concentrations (1M) perovskite precursor ink consists of DMF and DMSO solvents.

Figure S6

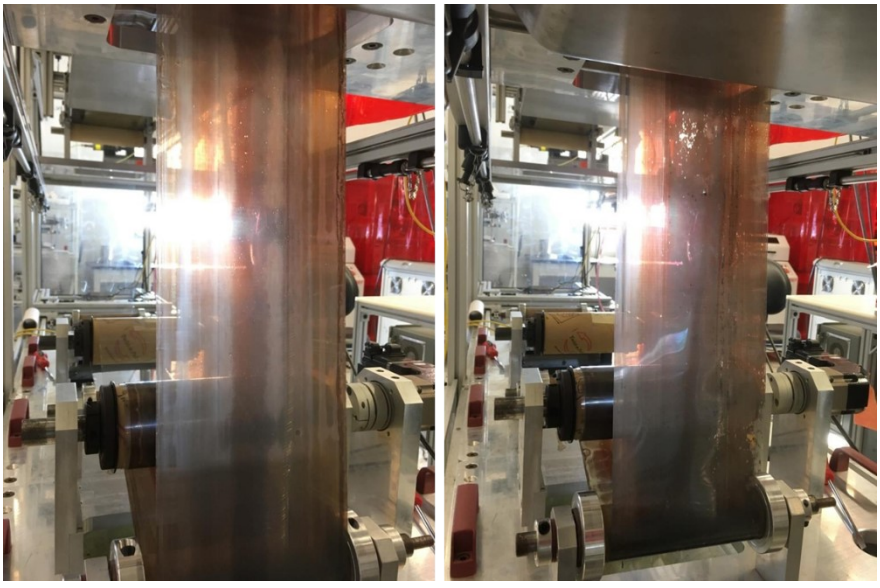


Figure S6: Optical images of roll-to-roll deposited perovskite films from lower concentrations (0.5M) perovskite precursor ink consists of DMF and DMSO solvents.

Figure S7

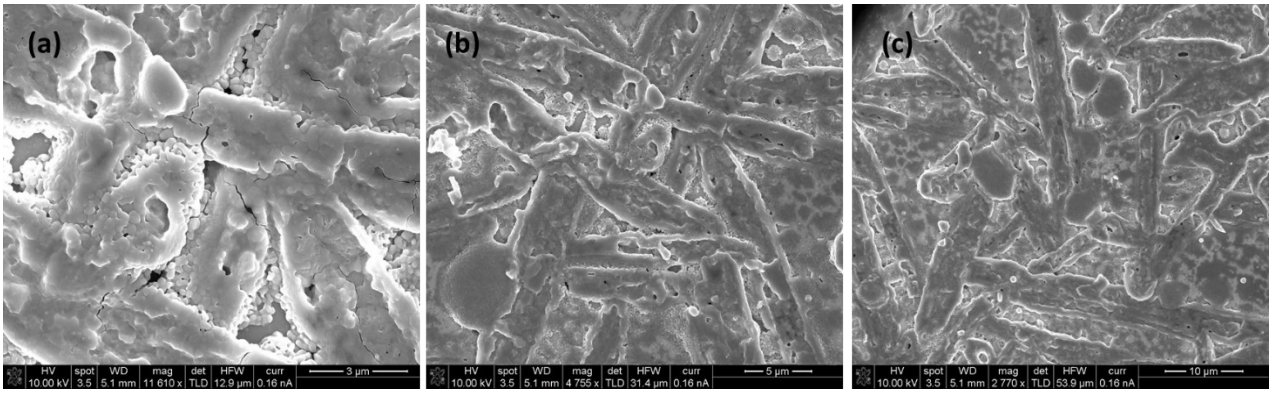


Figure S7: SEM images of roll-to-roll deposited perovskite films from lower concentrations (0.5M) perovskite precursor ink consists of DMF and DMSO solvents.

Figure S8

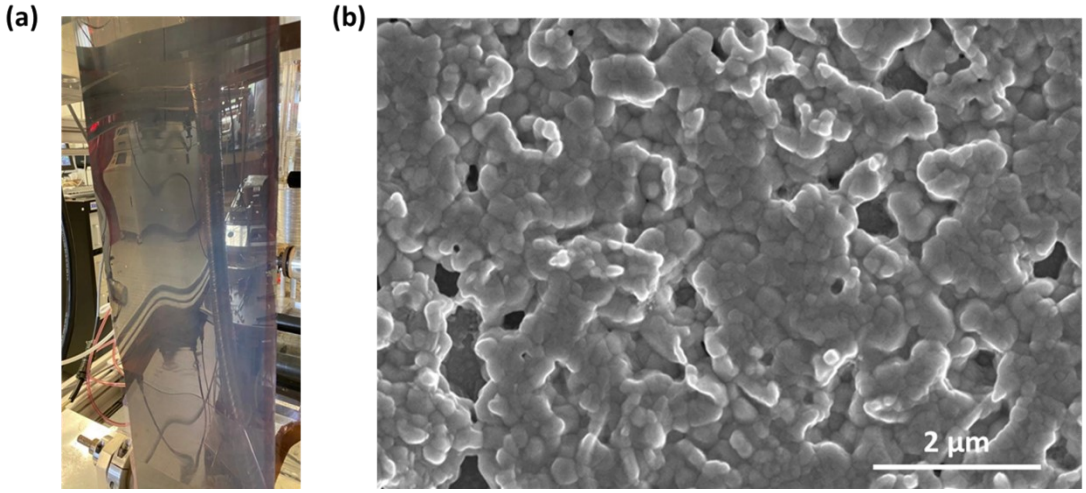


Figure S8: (a) Optical and (b) SEM images of roll-to-roll deposited perovskite films having precursor solvent ink consists of ACN and 2-MeOH solvents.

c) Roll-to-roll slot-die coating of perovskite at different web speeds:

By considering the ACN: 2-MeOH solvent system, different web speeds (1.5, 2, 2.5, 3 and 4 m/min) are explored to obtain a uniform, smooth and pinhole free perovskite films (Table S2). It was found that at higher web speeds (2.5, 3 and 4 m/min), the perovskite film formation is non uniform having large gaps over the substrate. The corresponding optical and SEM images of perovskite films are shown in Figure S9, with the increase of web speed in deposition, the morphology of perovskite films turned from crystals to a long needle dendritic network at higher speeds. It is attributed to improper drying of the as deposited wet perovskite films at higher speeds, resulting there is an incomplete drying of wet films, conversion of precursors and formation of intermediate products. It was found that at lower speeds (1.5 and 2 m/min), there is formation of uniform perovskite layer with high surface coverage and having minimal pinholes on the film. This is ascribed to facilitating sufficient time to allow the drying of the as deposited perovskite film, which has positive effect on the crystallization process, resulting in densely packed uniform perovskite layer.

Table S2

Deposition of perovskite at a constant web speed of 1.8 M/min		Deposition of perovskite at a constant flow rate of 1.6 ml/min	
Flow rate (ml/min)	**Average Thickness (nm)**	**Web speed (M/min)**	**Average Thickness (nm)**
1.2	400 ± 21	1.5	1100 ± 28
1.5	550 ± 16	1.8	940 ± 21
1.6	630 ± 19	2.0	820 ± 14
1.8	780 ± 11	2.5	700 ± 25
2.0	1020 ± 22	3.0	560 ± 22

Table S2: The variation in the thickness of roll-to-roll slot-die coated perovskite layer by changing different flow rates and web speeds.

Figure S9

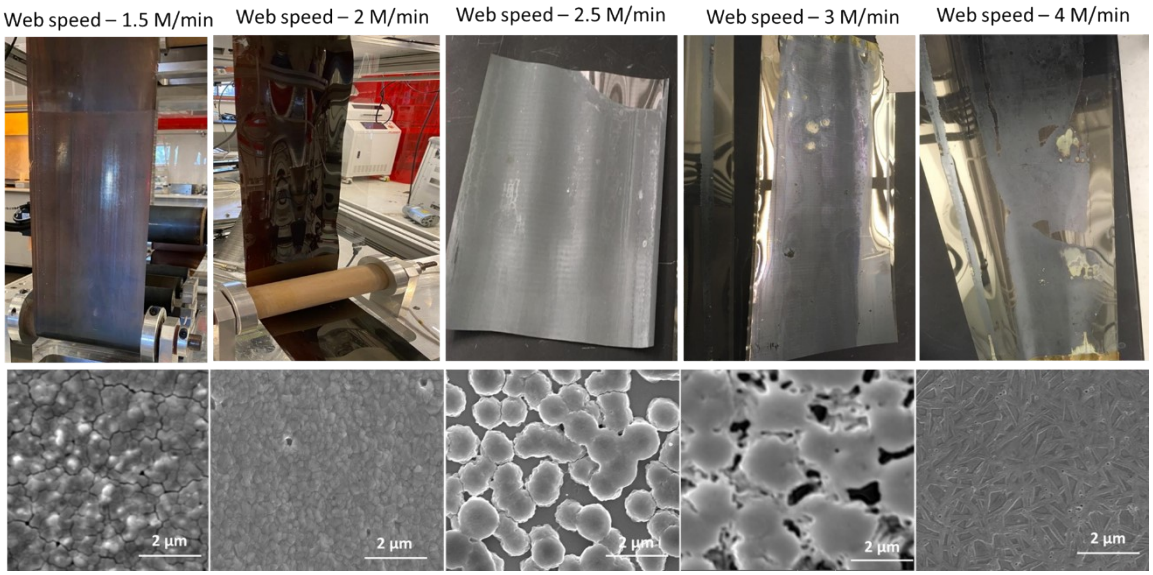
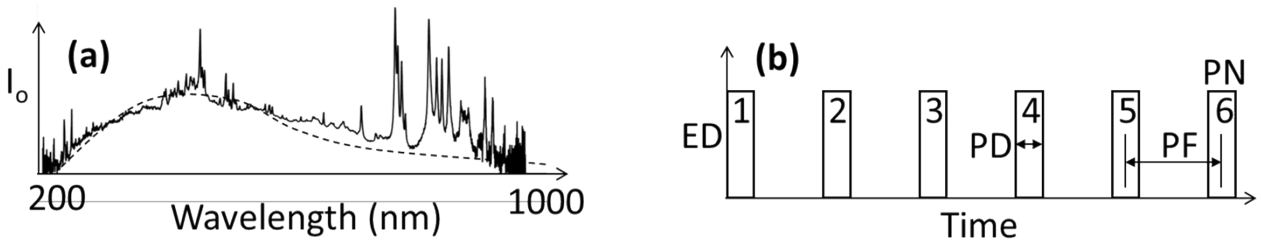


Figure S9: Optical and SEM images of roll-to-roll deposited perovskite films at different web speeds.

Figure S10



PF – Pulse Frequency, PD – Pulse Duration
ED – Energy Density (I_o), PN – Pulse Number

$$PN = \frac{Lamp\ length}{web\ speed} PF$$

Figure S10: a) optical output of the IPL lamp, and b) Pulse operation on a continuous web and calculation of the number of pulses per section of web.