# Supplementary Information

# Transferrable Optimization of Spray-Coated PbI<sub>2</sub> Films for Perovskite Solar Cell Fabrication

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# The Coffee Stain Effect in Spray Coated PbI<sub>2</sub> Films



Figure S1 Optical transmission image of sparsely deposited droplets of  $PbI_2$  films in DMF on  $TiO_2$  surface (droplets were allowed to dry, leaving only  $PbI_2$  on the surface). Droplets do not form a wet film due to large spacing between droplets, but clearly demonstrate the tendency of  $PbI_2$  to accumulate at droplet edges due to the coffee stain effect. The scale bar is 100  $\mu$ m.

## Direct Measurement of the Evaporation Rate of a Liquid Film

The evaporation rate of a liquid film can be measured directly by placing a high precision digital scale inside the spray process chamber and dispending a small volume of solvent over a substrate with known area. If the wetting of the substrate by the solvent is near perfect (as is the case for DMF over TiO<sub>2</sub>) the solvent will cover the substrate completely. If the wet film is sufficiently thin, the area of the wet film will be close to equal to the area of the substrate. Figure S2 (a) shows optical images of wet film profile for different amounts of liquid dispensed on a 15 × 15 mm substrate. Comparing thickness of the wet film in the center of the substrate to thickness obtained assuming that the wet film is completely flat (Figure S2b), we see that at less than 40  $\mu$ L on a 15 × 15 mm substrate the film is effectively flat.



Figure S2 (a) Wet film profile with 35  $\mu$ L (above) and 100  $\mu$ L (below) of DMF dispensed over 15 × 15 mm substrate. Scale bar is 0.1mm. (b) Wet film thickness at the center of a square 15 × 15 mm substrate as a function of dispensed volume. Dots are experimental measurements, straight line is thickness computed assuming uniform liquid distribution. (c) Rate of change of mass of a wet film of 50 × 50 mm inside the spray chamber. Liquid is dispensed at 0 min. Red line is linear fit between 5 and 60 min, evaporation rate is 81.76  $\mu$ g s<sup>-1</sup>cm<sup>-2</sup>. Deviation from linear evaporation rate is observed when the film de-wets and evaporation area is no longer equal to area of the substrate.

To relate the measured rate from mass change on a sample with known area, to a sample that has been spray coated with solvent, it is necessary to consider that evaporation rate at film edges is faster than far from edges. Spray coating covers an area that exceeds the sample edges, so the average evaporation rate from a sample that was spray coated will be lower than from a sample that was covered with liquid exactly to the edges. To determine the evaporation rate for a surface that matches the shape of the spray, local evaporation rate was computed using COMSOL Multiphysics 5.2 software. Evaporation was modeled by constraining the concentration of evaporating species to match the saturation pressure across the evaporating surface and computing the flux of evaporating species, with appropriate temperature and air flow distributions. Air flow distribution in a realistic geometry is very difficult to compute, therefore it is approximated by a laminar flow set to achieve an experimentally measured evaporation rate.

Figure 4 (main text) shows the computed difference between evaporation rates at sample edges and center. Simulation indicates that average evaporation rate for a  $15 \times 15$  mm area at the center of a  $50 \times 50$  mm surface of evaporating liquid surface is 0.75 of the rate averaged over the entire liquid surface (including the edges).

#### **Computation of Evaporative Mass Transfer Coefficient**

Knowing the evaporation rate of a solvent allows us to compute evaporative mass transfer coefficient that is characteristic of the process chamber. Once the mass transfer coefficient is known, it can be used to predict evaporation rates of any solvent with known saturation pressure (temperature dependent) and diffusivity in air.

Evaporation from a liquid surface far from the boiling temperature can be modeled as follows:<sup>[S1]</sup>

$$C = C_m \left(\frac{P_{sat}(T)}{2} - \frac{P_{inf}}{RT}\right)$$

Where C is the evaporation rate in mol/(s m<sup>2</sup>),  $C_m$  is the evaporative mass transfer coefficient,  $P_{sat}$  is the solvent saturation pressure close to liquid surface, and  $P_{inf}$  is the solvent partial pressure at infinity, R is the ideal gas constant, and T is temperature (in K). This model is appropriate to situations where a thin layer of saturated vapor is always maintained on the surface of the liquid. It is also assumed that the evaporation rate is sufficiently low that no appreciable temperature gradient develops inside the liquid film, i.e. the temperature of the liquid film is equal to the temperature of the substrate. This assumption was numerically verified for relevant temperatures and evaporation rates. For liquids where evaporation causes appreciable cooling of the substrate, correction to substrate temperature can be computed (see below).

The evaporative mass transfer  $C_m$  can be written as<sup>[S1]</sup>

$$C_m = \frac{Sh D}{L}$$

Where Sh is the dimensionless Sherwood number, D is diffusivity of the evaporating species in air, and L is a characteristic length. Computation of the Sherwood number depends on whether the air flow is dominated by forced or free convection of air. Forced convection refers to air motion that is created mechanically, for example by exhaust flow, whereas free (or buoyant) convection is generated by density gradients. For the purpose of this work it is assumed that density variations are dominated by thermal expansion of air due to heating. Chief difference between forced and free convection is that mass transfer coefficient due to forced convection can be expected to be close to constant with temperature, whereas free convection coefficient will strongly depend on temperature differences in the system.

In the case of forced convection Sherwood number can be expressed as  $Re = C Re^a Sc^b$  where Re is Reynolds number, Sc is Schmidt number, and a,b,c are constants.<sup>[S1]</sup> In the relevant temperature range (25-70C) Reynolds and Schmidt numbers vary negligibly compared to variations in vapor saturation pressure, therefore mass transfer coefficient due to forced convection can be considered temperature independent.

By analogy with Nusselt number, Sherwood number for free convection can be written as  $Re = C Ra^a$  where Ra is the Rayleigh number and a, c are constants. Raleigh number for mass transfer is defined as Ra = Gr Sc, where Gr is the Grashoff number and Sc is Shemidt number. Defined as follows:

$$Gr = \frac{\rho^2 g\alpha}{\mu^2} \Delta T L^3$$
$$Sc = \frac{\mu}{\rho D}$$

Where  $\rho$  is fluid density, g - gravity constant,  $\alpha$  - coefficient of thermal expansion,  $\mu$  - dynamic viscosity,  $\Delta T$  relevant temperature difference, L - characteristic length scale, and D - diffusivity of the evaporating species in air. In the relevant temperature range (25-70°C), the only significant temperature dependence is contained in the  $\Delta T$  term, the other terms are fixed by material properties or geometry.

Computing the value of Raleigh number gives a value between 1e7 and 2e7 for temperatures between 30 and 70°C, therefore the relevant relationship to Sherwood number is  $Sh = 0.15 Ra^{1/3}$ , for top side of a heated horizontal plate).<sup>[S1]</sup>

To compute the free convection mass transfer constant, taking material properties to be constant, we can write:

$$C_{free} = 0.15 \frac{D^{2/3} (\Delta T)^{1/3}}{L} \left(\frac{\rho^2 g \alpha}{\mu^2} L^3 \frac{\mu}{\rho}\right)^{1/3} = \frac{D^{2/3} (\Delta T)^{1/3}}{L} A$$

Where A contains material and temperature independent terms, D is diffusivity of evaporating species, and L is a characteristic length.

To adjust for specific geometry of the process chamber the 1/L factor can be used as a fitting parameter. Figure 3f (main text) shows the fit of drying rate measured by laser scattering to the model described above. Value at 24°C (no heating) is independently confirmed by direct mass change measurement. Where heating is applied, a single factor is applied as a fitting parameter, to account for specifics of chamber geometry. Note that the same value of the fitting parameter was used for all evaporation rates shows in Figure 3f (narrow spray DMF, broad spray DMF, narrow spray IPA).

When both free and forced convection are significant the combined Sherwood number can be approximated as (the same relationship applies to mass transfer constants):<sup>[S1]</sup>

$$Sh^3 = Sh^3_{forced} + Sh^3_{free}$$

From this relationship it is clear that the evaporation rate will be dominated by either forced or free convection term, unless they are very close to equal.

**Nozzle-Free Ultrasonic Spray Coating** 



*Figure S3 Nozzle-free ultrasonic spray coating. Ink is applied to coating head that vibrates at 35kHz to atomize the liquid. Carrier gas flow directs atomized ink toward the coating substrate.* 

#### **Estimation of Diffusivity**

Diffusivity of evaporating species in air needs to be known to estimate evaporation rate. Diffusivity values for many substances have been measured, however, in the cases when a value is not available, diffusivity of a substance can be estimated from its molecular mass.<sup>[S2]</sup>

$$D_{B,air} = D_{A,air} \left(\frac{M_A}{M_B}\right)^{1/2}$$

Where  $D_{A,air}$  is a known diffusivity of a substance with molecular mass  $M_A$  and  $D_{B,air}$  is an unknown diffusivity of a substance with molecular mass  $M_B$ . Examination of the available data (Figure S4) shows that diffusivities of organic solvents with molecular mass close to DMF and DMSO do not vary strongly, and approximately follow the dependence on the molecular mass shown above.

Diffusivity of DFM and DMSO was estimated by fitting a known diffusivity values to  $D = C(1/M)^{1/2}$ , where D is diffusivity, m is molar mass, and C is a fitting parameter. Obtained values are shows in Table S1.



Figure S4 Diffusivity values for various substances (at 25C, 1 atm), available in literature. Color of points denotes the source Incropera<sup>[S1]</sup>,  $Lugg^{[S3]}$ , or Dickhut<sup>[S4]</sup>. Red line marks a fit to data by  $D = A M^{-0.5}$ , where D is diffusivity, A is a fitting parameter, and M is molecular mass. Black square marks the expected value of DMF diffusivity based on molecular mass.

Substance	Molar Mass	Estimated Diffusivity in Air
DMF	73.09 g mol <sup>-1</sup>	$8.7e-6 m^2 s^{-1}$
DMSO	78.13 g mol <sup>-1</sup>	$8.4 \text{ e-6 m}^2\text{s}^{-1}$

Table S1 Estimated diffusivity values from a fit to literature data.

#### Effect of Evaporative Cooling on Wet Film



Figure S5 Effect of evaporative cooling on wet film temperature. Temperature was computed at different times assuming wet film is initially at 24°C and glass substrate is at hotplate temperature. Slow evaporation of DMF produces deviation of less than 1C at 70°C, but IPA evaporation produces a substantial change in temperature after 10 seconds.

Substantial cooling of the substrate due to evaporation could affect evaporation rate. To quantify the effect of evaporative cooling, change of the wet film temperature was computed by taking into account heat loss to evaporation. Temperature dependent evaporation rates were obtained from the model described above. The system was modeled in COMSOL Multiphysics 5.2 in 1 dimension as a 2.2 mm thick glass substrate and 2  $\mu$ m thick wet film (DMF or IPA). Substrate temperature was fixed at the bottom, and the top of the liquid film was set as a heat sink corresponding to heat required for evaporation rate at given temperature.

### Independence of Perovskite Crystal Grain Size from Spray Conditions



Figure S6 AFM topography images of MAPbI<sub>3</sub> films produced by reaction with different cocentration of MAI-IPA solution. (a) 10 mg mL<sup>-1</sup>, (b) 7 mg mL<sup>-1</sup>, (c) 5 mg mL<sup>-1</sup>. Small changes in MAI concentration dramatically affect MAPbI<sub>3</sub> grain size. All samples were allowed to react for 2 min to reach saturation. Scale bars are 1  $\mu$ m. Gray scale indicates heigth for (a), (b) is 0 to 0.5  $\mu$ m, and for (c) is 0 to 1  $\mu$ m.

For sequential perovskite formation process, the grain size and (microscopic scale) surface coverage are largely determined by the concentration of MAI solution. The strong dependence of grain size and surface coverage on MAI solution concentration was first identified by Im et.

al.<sup>[S5]</sup>, who found that by varying MAI concentration between 5 mg mL<sup>-1</sup> and 10 mg mL<sup>-1</sup> it was possible to change grain size from less than 200 nm mean width to over 800 nm mean width. Larger grains generally result in better performance, however larger grains, in this case, are accompanied by larger spaces between grains, hence reduced surface coverage. Im et. al.<sup>[S5]</sup> found that optimal compromise between grain size and surface coverage is around 7 mg/mL MAI. In our testing, we closely reproduced this result (see Figure 6) therefore we chose to also use 7 mg/mL MAI solution in IPA.

Independence of MAPbI<sub>3</sub> grain size from PbI<sub>2</sub> spray conditions is important, because it allows a broad choice of conditions during coating of PbI<sub>2</sub>, without danger of affecting quality of MAPbI<sub>3</sub> formed in the following step. As long as required PbI<sub>2</sub> film thickness is achieved, optimization of PbI<sub>2</sub> coating process can be performed without considering MAPbI<sub>3</sub> formation.



#### **Device Steady State Performance**

Figure S7 Steady state performance of two example solar cells incorporating spray coated  $MAPbI_3$  layer. Cell fabrication process was the same as for cells shown in main text. Solar cell active area is  $1.1 \text{ cm}^2$ . Cells were measured continuously by drawing maximum power (with maximum power point tracking), under 1 sum illumination. During measurment cells were in a dry nitrogen atmosphere.

#### **Device Performance and Dependence of Process Parameters**



Figure S8 Example of performance dependence on  $PbI_2$  wet film thickness in the spray coating process. Lower wet film thickness is correlated with better film uniformity (Figure 1, 2, main text) and better performance as seen in this figure. Devices were fabricated as described in the experimental section. 3 devices (active area  $1.1 \text{ cm}^2$ ) were fabricated for each data point, error bars show standard deviation.



Figure S9 IV characteristics of a perovskite solar cell module fabricated using the spray coating process. Individual device active area is  $2 \text{ cm}^2$ . Total active area of the module is  $10 \text{ cm}^2$ . (a)-(e) Individual device IV characteristics, forward (black, closed squares) and reverse (red, open squares) sweep. Forward (F) and Reverse (R) sweep PCE values are given for each device. (f) IV characteristic of the modules (5 devices connected in series). Forward (F) and Reverse (R) sweep PCE values are given in the figure. The inset shows the photograph of the finished module. The module was fabricated and characterized as described in the experimental section.

#### References

#### Large Area Device Performance

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