Supporting Information

Nucleation and Crystal Growth of Organic-Inorganic Lead Halide Perovskites under Different Relative Humidity

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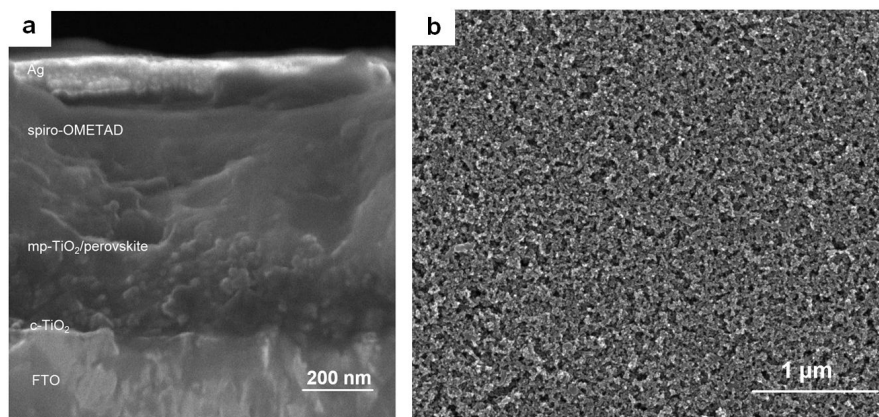
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Figure S1. (a) SEM cross-sectional image of $CH_3NH_3PbI_{3-x}Cl_x$ device. The layers from the bottom are:

FTO, c-TiO$_2$, mp-TiO$_2$/perovskite, spiro-OMETAD, Ag. (b) SEM image of mp-TiO$_2$ substrate.
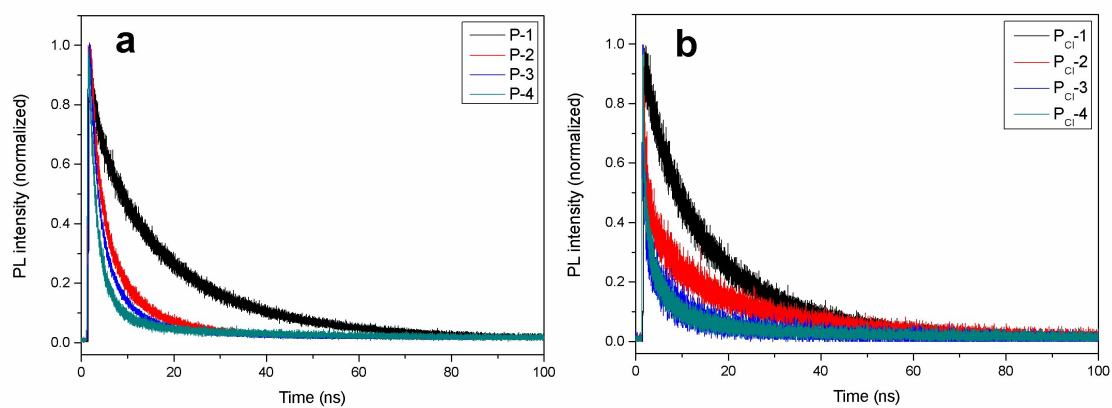

Figure S2. Time-resolved PL decay curves of (a) $CH_3NH_3PbI_3$ and (b) $CH_3NH_3PbI_{3-x}Cl_x$ films prepared

under different humidity conditions.

(a) solution, nucleus, σ_0, σ_1, σ_2, substrate, r, 2θ
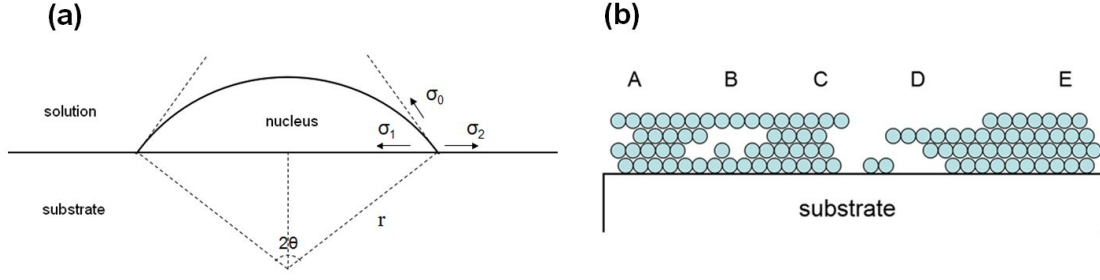
(b) A, B, C, D, E, substrate

Figure S3. (a) Spherical cap nucleus formed on substrate surface; (b) The difference of supersaturation in different regions (A,C,E > B, D) results in destruction of crystal structure.[3]

Assuming that spherical cap nucleus is formed on substrate surface (Fig. S3a),[1] we define r as nucleation radius, θ as contact angle of nucleus and substrate, ΔG_v as volume free energy per unit, σ_0 as nucleus surface tension, σ_1 as nucleus and substrate interface tension, σ_2 as substrate surface tension.

Under the equilibrium state, $\sigma_0 \cos\theta = \sigma_2 - \sigma_1$

The change of surface and interface free energy can be expressed as follows:

$$\Delta G_S = 2\pi r^2(1-\cos\theta)\sigma_0 + \pi(r\sin\theta)^2(\sigma_1 - \sigma_2)$$

$$= \pi r^2 \sigma_0 (2 - 3\cos\theta + \cos^3\theta)$$

For the spherical cap nucleus, its volume $V = \dfrac{\pi r^3(2-3\cos\theta+\cos^3\theta)}{3}$

So the change of volume free energy

$$\Delta G_V = V \cdot \Delta G_v = \frac{\pi r^3(2-3\cos\theta+\cos^3\theta)}{3}\Delta G_v$$

The change of total free energy

$$\Delta G = \Delta G_S + \Delta G_V = \pi(\frac{r^3}{3}\Delta G_v + r^2\sigma_0)(2-3\cos\theta+\cos^3\theta)$$

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Set $\dfrac{\partial(\Delta G)}{\partial r} = 0$, we can conclude the critical nucleus radius:

$$r_0 = \frac{-2\sigma_0}{\Delta G_v}(\Delta G_v < 0)$$

If ΔG_v is seen as the energy needed from equilibrium state to supersaturation , it can be

expressed as $\Delta G_v = -Z(T) \cdot \ln(\dfrac{\rho_s}{\rho_e}) = -Z(T) \cdot \ln(\xi + 1)$, in which $Z(T)$ is a temperature

dependent coefficient.[1] So the **critical nucleus radius** can be expressed as

$$r_0 = \frac{2\sigma_0}{Z(T)\ln(\xi + 1)} \;.$$

The growth type of thin film also depends on the Young's relationship of the interface

tensions:[2]

$$\text{Layer growth} \quad \sigma_2 \geq \sigma_0 + \sigma_1 + \frac{\Delta G_v}{C}$$

$$\text{Island growth} \quad \sigma_2 < \sigma_0 + \sigma_1 + \frac{\Delta G_v}{C}$$

C is a coefficient corresponded to crystal structure. So increased supersaturation is better for
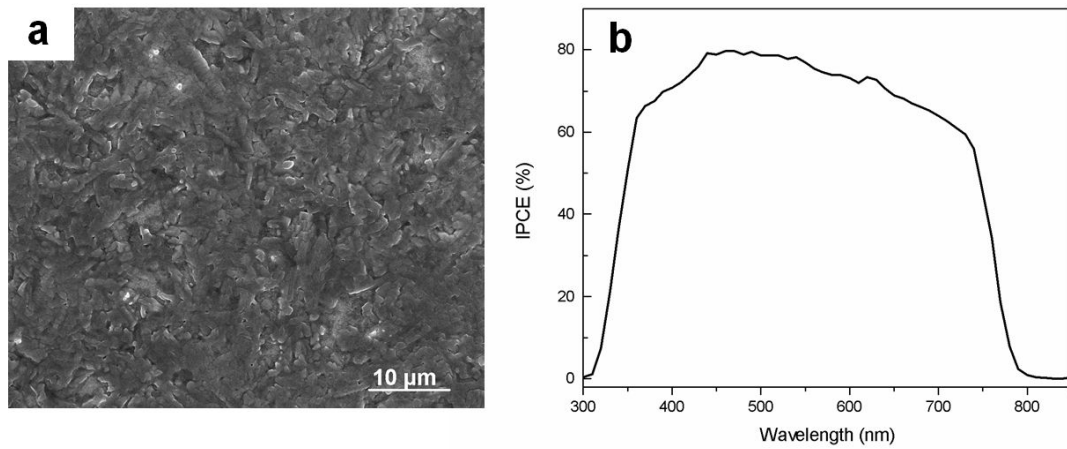
layer growth.

Figure S4. (a) SEM image of $CH_3NH_3PbI_{3-x}Cl_x$ film spin-coated under RH~10% and annealed under

RH~70%. (b) IPCE of the corresponding devices.

Table S1: Photovoltaic parameters measured under AM1.5 illumination of a batch of ten devices based on $CH_3NH_3PbI_{3-x}Cl_x$ films spin-coated under RH~10% followed by annealing under RH~70%.

Cell	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	PCE (%)
1	0.89	19.1	0.59	10.0
2	0.86	18.7	0.57	9.2
3	0.89	19.6	0.60	10.5
4	0.90	19.5	0.54	9.4
5	0.88	18.5	0.58	9.5
6	0.87	18.6	0.60	9.7
7	0.89	18.9	0.58	9.8
8	0.88	19.8	0.59	10.3
9	0.89	19.5	0.58	10.1
10	0.90	19.1	0.57	9.8
Average	0.88 ± 0.02	19.1 ± 0.6	0.58 ± 0.03	9.9 ± 0.5

References

1. Venables, J. A. *Introduction to Surface and Thin Film Processes*, World Publish

Corporation, Beijing, **2003**.

2. Aliofkhazraei, M.; Ali, N. *Two-Dimensional Nanostrusture*, CRC Press (an imprint of

Taylor & Francis Group), Boca Raton, **2012**

3. Zhang, K. C.; Zhang, L. H. *Crystal Growth (in Chinese)*, Science Press, Beijing, **1981**.