Supporting Information

Thermodynamic Regulation of $CH_3NH_3PbI_3$ Crystal Growth and Its Effect on Photovoltaic Performance of Perovskite Solar Cell

Namyoung Ahn [1†], Seong Min Kang[1†], Jin-Wook Lee [2], Mansoo Choi[1,*] and Nam-Gyu Park [2,*]

[1]Department of Mechanical and Aerospace Engineering, Seoul National University Seoul 151-742, Korea

[2]School of Chemical Engineering and Department of Energy Science Sungkyunkwan University, Suwon 440-746, Korea

Derive equation of thermodynamic $MAPbI_3$ reaction process.

From the relation (8) in the manuscript, we could derive a logarithmic formula by introducing constant C'.

$$lnY(grain\ size) = \frac{\hat{a}\hat{}\dagger G_c}{3kT} + C'$$

Substituting equation (7), we could derive a formula about relationship between grain size and concentration.

$$lnY = \frac{1}{3kT}\frac{32}{\left(\frac{kT}{V_M}ln\frac{C}{C_0}\right)^2} + C'$$

Finally, the equation could be obtained by replacing concentration C with X.

$$lnY = \frac{32\ddot{I}f_{sl}^{3}}{3kT(\frac{kT}{V_m}(lnX - lnC_0(T))^2} + C^{'}$$

Here, the equation was summarized as a simple formula with substitution other terms to constant, except for concentration.

$$lnY = \frac{B}{(lnX - A)^2} + C$$

It would be assumed that the equilibrium concentration is 0.02 M of MAI solution at room temperature since the PbI_2 film could not react with 0.02 M of MAI solution. In this manner, a value of A would be -3.19, which means natural log value of equilibrium constant. The other value of B and C were mathematically evaluated in order that the model was fitted with an actual data in Table S1, as result, B and C were 1.22 and 3.73 respectively (see Figure 3).

Table S1. Grain sizes, short-circuit photocurrent density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and power conversion efficiency (PCE) versus $MAPbI_3$ concentration. Data were taken from reference S1.

MAI Concentration	0.038 M	0.044 M	0.050 M	0.057 M	0.063 M
Grain Size (nm)	720	360	190	130	90
J_{sc} (mA/cm^2)	21.68	-	21.01	-	19.27
V_{oc} (V)	1.065	-	1.090	-	1.080
FF	0.709	-	0.711	-	0.646
PCE (%)	16.36	-	16.27	-	13.45

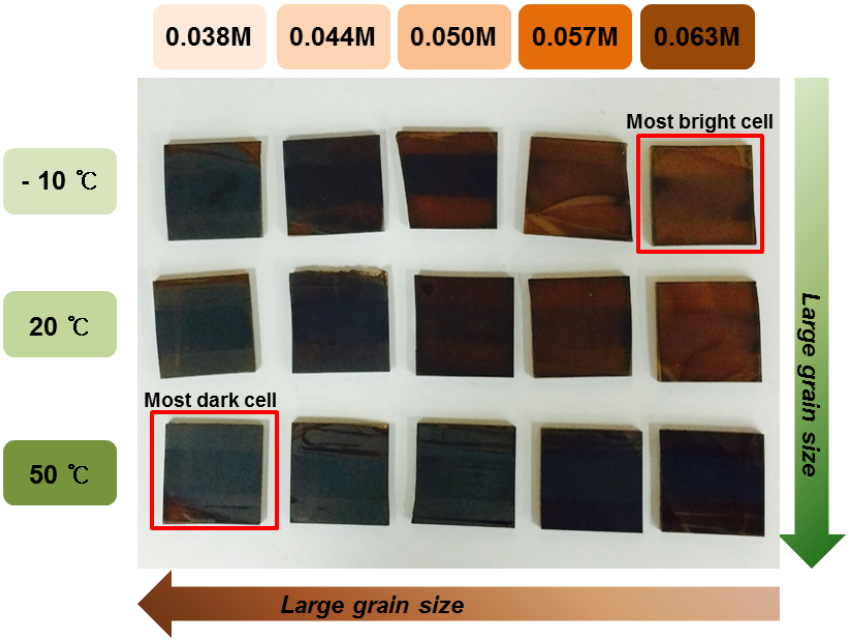

Figure S1. Photograph of $MAPbI_3$ coated substrates depending on MAI concentrations and reaction temperature.

References

S1. J.-H. Im, I.-H. Jang, N. Pellet, M. Grätzel and N.-G. Park, *Nat. Nanotechnol.*, 2014, **9**, 927-932.