Supplementary Information

Photo-enhanced Growth of Lead Halide Perovskite Crystals And Their Electro-optical Properties

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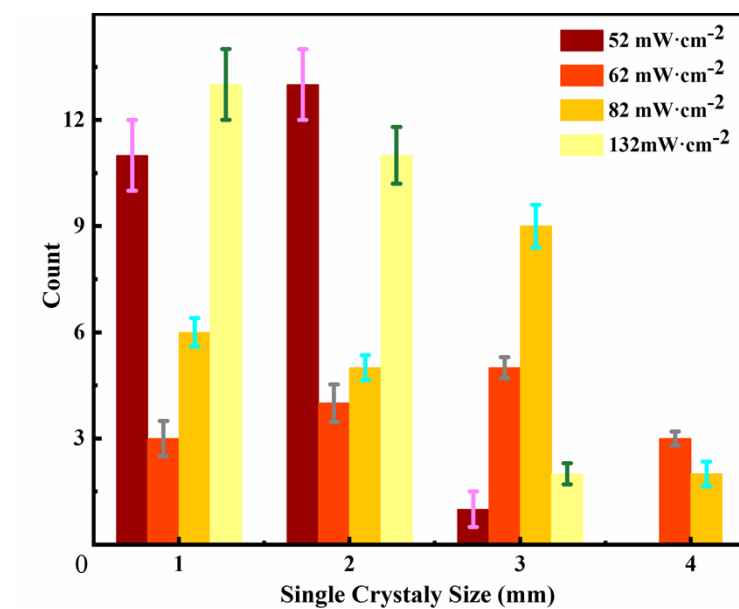
Results and Discussion

Figure S1 Statistics of the count and size of MAPbI$_3$ single crystals grown from the precursor solution under illumination with the optical power density of 52 mW • cm^{-2}, 62 mW • cm^{-2}, 82 mW • cm^{-2}, 132 mW • cm^{-2}.
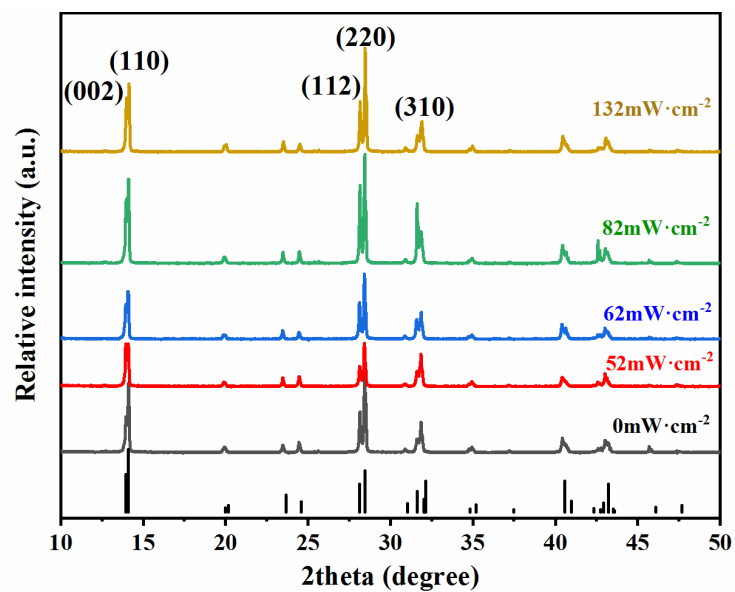
Figure S2 X-ray diffraction curves of MAPbI$_3$ powder grown from precursor solutions under illumination. The peaks at 14.2° and 28.6° has corresponded to the (110) and (220) planes of tetragonal structure for the MAPbI$_3$ single crystal. The peaks of the MAPbI$_3$ single crystal obtained under different conditions are almost the same and in good agreement with previously reported data (below). Therefore, it can be concluded that the introduction of external light outside does not affect the composition of the MAPbI$_3$ single crystal.
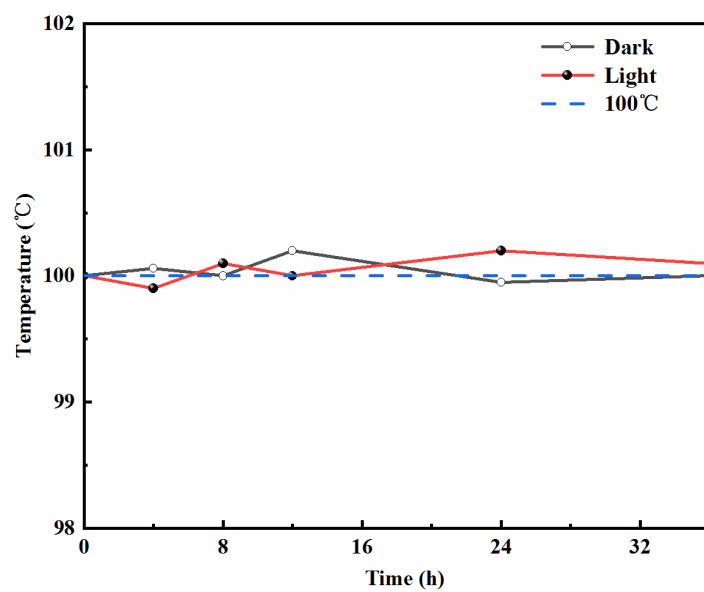
Figure S3 Temperature of the precursor solution measured at different times in the light (62 mW · cm^{-2}) and dark conditions. (It should be noted that the maximum temperature difference is 0.3° C which can be ignored)

Supplementary Note 1

The specific derivation process of equation (1) and equation (2):

Calculate the change in the free energy $\Delta\varphi$ when the volume is r solidified. When changing from liquid to solid, the change in free energy is: $\Delta F = F_{solid} - F_{liquid}$, and interface energy (S) between melt and nucleus is $S = \beta_2 r^2$. All changes in free energy nucleus shape remain unchanged. Thus

$$\Delta G = \beta_1 \Delta F r^3 - \beta_2 \alpha r^2 \qquad\qquad (S-1)$$

where β_1 and β_2 are the shape factors used to calculate the nucleus volume and the surface. α is the surface tension between the liquid and the solid. The second part of the equation is always a positive value. (In some cases, when the nucleation occurs on external impurities, the surface energy may be a negative value.)

According to the conditions for forming a stable crystal nucleus, only when $r > r_k$, the crystal nucleus will continue to grow because this action will cause a decrease in the free energy ΔG . r_k is defined as the critical crystal nucleus.

The critical nucleus size r_k can be obtained from the maximum value

$(\Delta G_{(r_k)} = 0)$ of the function $\Delta G_{(r)}$. Therefore

$$r_k = -2\beta_2 \alpha / 3\beta_1 \Delta F \qquad\qquad (S-2)$$

For a spherical nucleus with radius r ($\beta_1=4\pi/3$, $\beta_2=4\pi$) and a polyhedron of length 2r ($\beta_1=8$, $\beta_2=24$):

$$r_k = \frac{2\alpha}{|\Delta F|} \qquad\qquad (S-3)$$

It can be gotten from the formula (6-4) when $T \to T_0$ leads to $r_k \to \infty$. Therefore, the crystal will form when it is sub-cooled.

In the function of super-cooling ΔT , when the undercooling is not large, the free energy difference ΔF will be determined by using the following formula. At the melting temperature, $F_{solid} = F_{liquid}$, therefore:

$$F_{solid}(T) - F_{liquid}(T) = \left[F_{solid}(T) - F_{solid}(T_0) \right] - \left[F_{liquid}(T) - F_{liquid}(T_0) \right] \qquad (S-4)$$

The formula is decomposed into power series. When the degree of undercooling is not too large, $\Delta T = T_0 - T$ can be defined as the first item in these series:

$$F_{solid}(T) - F_{solid}(T_0) = \frac{\partial F_{solid}}{\partial T}(T - T_0) \qquad\qquad (S-5)$$

$$F_{liquid}(T) - F_{liquid}(T_0) = \frac{\partial F_{liquid}}{\partial T}(T - T_0) \qquad\qquad (S-6)$$

$$F_{solid}(T) - F_{liquid}(T) = \left(\frac{\partial F_{solid}}{\partial T} - \frac{\partial F_{liquid}}{\partial T} \right)(T - T_0) = \left(S_{liquid} - S_{solid} \right)(T - T_0) \qquad (S-7)$$

Because of $\dfrac{\partial F}{\partial T} = -S$, where S is the entropy of the system. Crystalline latent heat (Q) $Q = -T_0 \Delta S$ is quoted, so:

$$F_{solid}\left(T\right) - F_{liquid}\left(T\right) = \frac{Q}{T_0}\left(T - T_0\right) \tag{S-8}$$

$$\Delta F = -\frac{\Delta TQ}{T_0} \tag{S-9}$$

From equation (S-1) and (S-9), we get:

$$r_k = \frac{2\alpha\beta_2 T_0}{3Q\Delta T\beta_1} \tag{S-10}$$

The nucleation energy of the nucleus with a size of r_k is:

$$\Delta G^* = \frac{4\beta_2^3\alpha^3 T_0^2}{27\beta_1^2 Q^2 \left(\Delta T\right)^2} \tag{S-11}$$

According to Lippmann`s classical equation:

$$\frac{d\alpha}{dE} = -q \tag{S-12}$$

which is important for and confirmed by wetting phenomena at the solid-liquid interface, it is expected that r varies with the square of the charge density q:

$$\alpha - \alpha_0 = -\frac{q^2}{2C_0} \tag{S-13}$$

where C0 is the double-layer capacitance. From the above formula we can get:

$$\Delta G^* = \frac{\beta_2^3 T_0^2 \left(2C_0\alpha_0 - q^2\right)^2}{54C_0\beta_1 Q \cdot \Delta T} \tag{S-14}$$