Supporting information

Ultrafast Ion Migration in Hybrid Perovskite Polycrystalline Thin Films under Light and Suppressing in Single Crystals

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Computational details

Ion migration velocity *v* was deduced from the PbI_2 line migration speed L/t, where L is the PbI_2 line migration distance and t is the transit time. And based on v=μE, the mobility could be further calculated.

Conductivity σ was given by the formula σ=V*l*/IS, where V, I, *l* and S are the voltage, current, channel width, and current channel cross-section area, respectively.

The activation energy Ea is determined by the Nerst-Einstein relation $\sigma(T) = \frac{\sigma_0}{T} exp\left(\frac{-E_a}{kT}\right)$, where k, T refer to Boltzmann constant, temperature. And Ea is derived from the slope of the ln(σT)-1/kT relation.

According to the formula σ_{ion}=nqμ, conductivity of a material is determined by two factors: the concentration of free ions n and ions mobility μ. Both of them follow Arrhenius thermal-activation function, which could be expressed as

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$\sigma_{ion} \propto n_0 exp\left(-\frac{E1a}{kT}\right)\mu_0 exp\left(-\frac{E2a}{kT}\right)$, where E_{1a} and E_{2a} denote the free ions generation (concentration) activation energy and ion diffusion activation energy (or named as ion migration activation energy), respectively. The ion diffusion activation energy can be directly extracted from ion diffusion experiment.

Fick's second law predicts how diffusion causes the concentration to change with time, which in one dimension reads $\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$, where C, D, t, x are the concentration, diffusion coefficient, time and position, respectively. A simple solution of concentration C(x,t) with time t in x direction from a boundary x=0 is $C(x,t) = C_0 erfc\left(\frac{x}{2\sqrt{Dt}}\right)$. When $C=C_0/2$, $erfc\left(\frac{x}{2\sqrt{Dt}}\right)$=0.5, and then follows the equation $x = \sqrt{Dt}$. After applying the diffusion length and diffusion time into the equation, we could get diffusivity. And based on the Einstein relation $D=\mu k_B T$, the mobility μ could be given. As mentioned above, the mobility changes with temperature following the Arrhenius thermal-activation model. From the equation $\mu = \mu_0 exp\left(-\frac{E_a}{kT}\right)$, the ion diffusion activation energy Ea of Br^- could be calculated based on the mobilities acquired at two temperatures (RT and 50 ^oC).

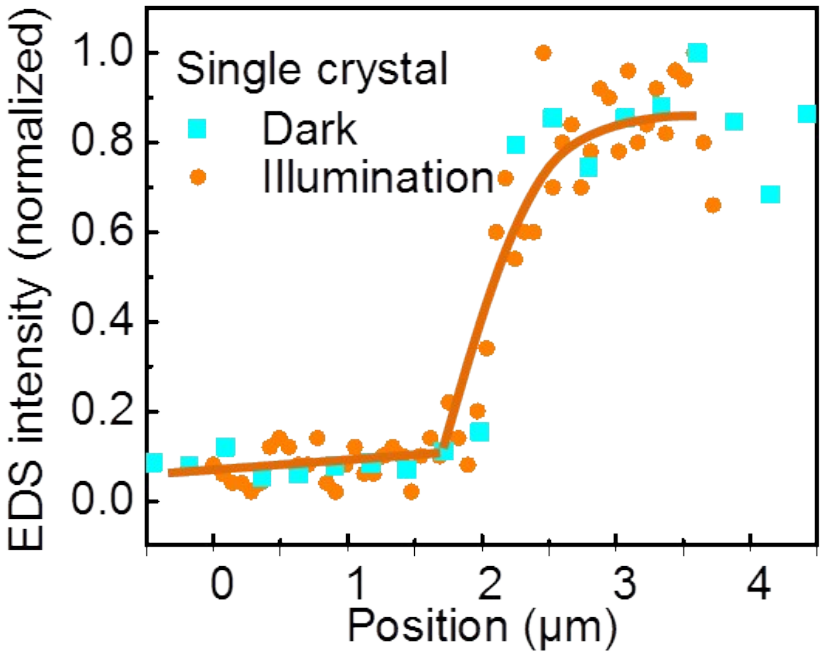

Figure S1 EDS line scan of Br^- diffusion on single crystal with or without 1 sun illumination for 48 hours.