Supplementary Information for

Grain Boundary Dominated Current Hysteresis and Ion Migration in Polycrystalline Perovskite Solar Cells

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Supplementary Figure 1: (a) Height and (b) deflection images of the perovskite sample before the $I$-$V$ measurement. (c) Height and (d) deflection images of the same area after the $I$-$V$ measurement. The blue squares and red triangles indicate where the $I$-$V$ measurements were performed at grain boundary and grain interior, respectively.
Supplementary Figure 2: (a) Topography AFM image of the perovskite thin film. Five locations where c-AFM tip was placed at to measure dark current are labeled with white triangles. (b)-(f) Dark curves measured at various points with an interval of \(~100\) nm in the direction from the center of a grain to the grain boundary (Δ1-Δ5 points as shown in the Supplementary Figure 2 (a)).

The results show that the dark-current hysteresis only appeared when the c-AFM tip placed with a range about 100 nm (Δ4 point) from the grain boundary for the 500-nm-thick perovskite film. This support our scenario that grain boundaries dominates the ion migration.
Supplementary Figure 3: Local dark-current measured on a grain with applying 43 nN (a), 82 nN (b) and 164 nN (c) loading force on the c-AFM tip, respectively. Local dark-current measured at a grain boundary (GB) with applying 43 nN (d), 82 nN (e) and 164 nN (f) loading force on the c-AFM tip, respectively.
Supplementary Figure 4: (a) Dark-current measured at GB showed a large built-in potential difference ($\Delta V_B$) with reverse and forward scanning, as a result of fast ion migration. (b) Dark-current measured in a grain showed negligible built-in potential difference ($\Delta V_B$) with reverse and forward scanning, as a result of slow ion migration. (c) Statistical results demonstrate that the $\Delta V_B$ difference between GBs and grains is well reproducible.
Supplementary Figure 5: Grains with textured structure in CH$_3$NH$_3$PbI$_3$ thin film.
Supplementary Figure 6: (a) A SEM image shows grains with different topography. (b) Diffraction pattern of a smooth grain. (c) Diffraction pattern of a textured grain.
Supplementary Figure 7: No dark current hysteresis was observed in the CH$_3$NH$_3$PbBr$_3$ single-crystal device regardless of the scanning rate: (a) 0.5 V s$^{-1}$, (b) 2 V s$^{-1}$, (c) 10 V s$^{-1}$.