The past 2 years have seen the uniquely rapid emergence of a new class of solar cell based on mixed organic–inorganic halide perovskite. Grain boundaries are present in polycrystalline thin film solar cell, and they play an important role that could be benign or detrimental to solar-cell performance. Here we present efficient charge separation and collection at the grain boundaries measured by KPFM and c-AFM in CH₃NH₃PbI₃ film in a CH₃NH₃PbI₃/TiO₂/FTO/glass heterojunction structure. We observe the presence of a potential barrier along the grain boundaries under dark conditions and higher photovoltage along the grain boundaries compare to grain interior under the illumination. Also, c-AFM measurement presents higher short-circuit current collection near grain boundaries, confirming the beneficial roles grain boundaries play in collecting carriers efficiently.

It is reported that GBs in these solar cells are electrically charged by impurities or different types of vacancies and create downward band bending toward the GBs in a p-type absorber.12–18 Thus, photogenerated electrons and holes near the GBs will be easily separated by the built-in field at the GBs, and the recombination rate of these carriers will be lower at the GBs. In some cases, it is suggested that in a p-type absorber the photogenerated electrons are flowing along the GB core by a downward band bending created near the GB and subsequently transported to the junction while the main route for photogenerated holes transport is within the grain interior.19 In organic–inorganic perovskite thin-film solar cells, the presence of high densities of grain boundaries does not appear to degrade their electrical performance. Yin et al.20 reported that GBs in CH₃NH₃PbI₃ are intrinsically benign based on first-principle calculations. GBs such as Σ3 (111) and Σ3 (111) do not generate deep states in the band gap. Edri et al.21,22 performed contact potential difference (CPD) mapping on GBs in CH₃NH₃PbI₃. It was shown that ~40 mV higher surface potential across the GBs was found in the dark and is reduced under illumination. Chen et al.23 reported that grain boundary potential can be controlled via passivation. By releasing the organic species during annealing of the film, higher surface potential at the GBs are changed from 50 mV to lower surface potential around 30 mV. It was suspected that carrier collections.12–18
PbI$_2$ phase is presented in perovskite GBs and passivates the GBs. Higher surface potential at the GBs in these studies can be due to band bending in the energy band diagram. However, it is still unclear how photogenerated charges behave at the GBs.

In this work, GBs of organic−inorganic halide perovskite films were characterized by Kelvin probe force microscopy (KPFM) and conductive-AFM (c-AFM) to investigate their role in a CH$_3$NH$_3$PbI$_3$/TiO$_2$ heterojunction device. Such a planar structure is chosen due to the demonstrated device performance potential, and its simple design allows the electrical properties at the GBs to be studied without the complication of the mesoporous-TiO$_2$. KPFM has been used as a tool to measure the CPD and the surface photovoltage (SPV), while c-AFM has been used to measure local photocurrent of thin films. These techniques allow direct measurements of spatial variations of charge-transport behavior of the thin-film device on the nanometer scale.

The sample we examined in this study was a CH$_3$NH$_3$PbI$_3$/TiO$_2$/FTO/glass heterojunction solar cell, as schematically illustrated in Figure 1. No capping layer or hole transport material (HTM) is deposited on top of the CH$_3$NH$_3$PbI$_3$ film such that the surface is directly accessible by the AFM probe. Detailed sample preparation methods are described in the Supporting Information. The thicknesses of CH$_3$NH$_3$PbI$_3$ and TiO$_2$ films are 300 and 50 nm, respectively.
Topography and CPD map of the underlying TiO₂ layer were also examined to ascertain the possible effect of the underlying TiO₂, as shown in Figure S1 in the Supporting Information. Both the topography and CPD images demonstrate uniform surface and work function across the TiO₂ layer, indicating that the topographical variance of the underlying TiO₂ layer does not affect the measured topography and CPD of the perovskite layer. The geometry of our experiment is described in Figure 1. For the KPFM setup (Figure 1a), the CPD measured is the CPD between the FTO layer and the gold probe tip. c-AFM measures short-circuit current using a gold probe, and a dc bias voltage was applied when required.

Figure 2a shows a spatial topography map of the surface of a CH₃NH₃PbI₃/TiO₂/FTO/glass heterojunction structure. As can be seen, the grains varying in size between 50 and 500 nm are found in these solar cell devices. Most of the grains are usually larger than the film thickness. Therefore, GBs are likely to be in direct contact with both the probe tip and the c-TiO₂ underlayer, as depicted in ref 6. Light I−V characteristics of the gold-coated solar device are shown in Figure S2 in the Supporting Information.

Figure 2b shows the CPD obtained in the dark where no excess charge should be generated. Therefore, the CPD should be constant across the film surface and correspond to the work function difference between the tip and the FTO. Any changes in CPD indicate the presence of an internal field inside the device. In Figure 2b, individual grains are clearly distinguishable and GBs have lower CPD values compared with the CPD within the grains. One possible reason is the presence of built-in potential around the charged GBs. At the GBs, interstitials and vacancies are present, and thus the polarity of GBs can be different compared with that within the grain interiors.24−26 GBs in perovskite oxides are often found to be depleted and form space-charge regions due to the existence of oxygen vacancies at the GBs.24−26

Figure 2c−e shows CPD maps under various illumination conditions of the same area. Figure 2f plots the average CPDs as a function of light intensities. The increase in CPD as a function of light intensity indicates that photogenerated carriers are efficiently separated at the CH₃NH₃PbI₃/TiO₂ heterojunction. Under open-circuit conditions, the diffusion current of charges away from the interface is balanced by photogenerated drift current caused by electric field built up in the device and the net current is zero. Therefore, a net CPD between the FTO anode and the perovskite surface can be obtained. The graph depicts a sublinear relationship between the CPD and the light intensity, which follows a similar relationship between the open-circuit voltage and the light intensity of the gold-coated HTM free device in Figure S2b in the Supporting Information. Such similar behavior ensures that our obtained SPV is correctly showing the open-circuit potential under illumination; in other words, the charge-separation process of the device using the AFM probe.

Under illumination, individual grains are also distinguishable as under the dark condition. However, it is apparent that the grain boundaries now have a higher CPD than the grain interiors that is opposite to what is observed under the dark condition. Figure 3c−f shows calculated SPV profiles obtained by subtracting CPD in the dark, where Figure 3c is from CPD under illumination at various intensities. The topography map in Figure 3a and line profile in Figure 3b are also shown for reference showing varying grain sizes and heights. In KPFM measurement, surface roughness can lead to CPD differences.

It is clear that the CPD maps in Figure 3 are attributed to the electrical features of the sample’s surface rather than the surface roughness. For instance, GB3, which has the lowest height (Figure 3b), does not have the lowest CPD (Figure 3c). As we’ve seen in Figure 3b, CPDs at the GBs are lower compared with those within the interior of grains under the dark condition. At the lowest intensity of 0.5 kW/cm², SPVs at the GBs 1, 2, and 3 are only a few millivolts higher compared with the SPV within the grain interiors. As the light intensity increases, SPVs at the GBs are enhanced and the SPV peaks at the GBs become more prominent with light intensity. This indicates that the photogenerated carriers are more effectively separated at the GBs compared with grain interiors. Such higher SPVs at the GBs could be attributed to broadening of bandgap at the GBs.27 According to first-principle calculations, valence band maximum (VBM) of CH₃NH₃PbI₃ antibonding s−p has the strongest coupling at the perovskite O₈ symmetry. If the symmetry is lowered at the GB, the coupling becomes weak and the antibonding state (VBM) drops and enlarges the bandgap.12

Photocurrent mapping was performed using c-AFM in contact mode to confirm that GBs act as efficient charge separator, which is shown in Figure 4. In the dark, there is no noticeable current observed as shown in Figure 4b, indicating a negligible effect of topography on current image. In this case,
the measured current is in the range of −1 to +1 pA, which is at the same level as the background noise from the instrument. When light with a wavelength of 500 nm is shone onto the sample with an intensity of 1.1 kW/cm², a sizable short-circuit current with highest magnitude of −53 pA was measured, as shown in Figure 4c. It is clear that the current is not evenly distributed over the surface of the film. Rather, the current is most prominent around the GBs, as shown in the overlapped c-AFM and topography maps in insets of Figure 4c,d. When a forward bias of 0.3 V is applied, the magnitude of the current is decreased to −33 pA, as shown in Figure 4d, but is still confined in the vicinity of the GBs, as depicted in insets of Figure 4c,d. One may expect that the higher current around GBs could lead to reduction of open-circuit voltage by creating shunting path. In fact, numerical simulations on GBs of CIGS solar cells demonstrated that open-circuit voltage could be higher or lower depending on the potential barrier height at GBs.28 Our KPFM results showed higher SPV at the GBs, and thus we suspect that the potential barrier formed in our perovskite sample does not lead to reduction of open-circuit voltage.

Figure 5 shows a line profile of a topography that crosses three GBs. The result shows that there is no direct correlation between the magnitude of the measured current and the height. For example, no short-circuit current is measured in the vicinity of GB2 where there is a dip in the film thickness. Not all GBs behave the same and are affected by crystallography and defect chemistry.12

The higher current collection near GBs is consistent with our previous KPFM results, which indicate that photogenerated carriers are more efficiently separated and transported along the GBs. On the basis of our KPFM results, lower CPD at the GBs under the dark condition implies that downward band bending is present at GBs. Although there are studies on the polarity of the CH₃NH₃PbI₃ films, which is determined by different types of vacancies,29,30 it is not yet known what type of vacancies could possibly be present at the GBs of polycrystalline CH₃NH₃PbI₃ films that charge the GBs and promote efficient charge separation.

We have demonstrated that the GBs in CH₃NH₃PbI₃ film in a CH₃NH₃PbI₃/TiO₂/FTO/glass heterojunction structure play a beneficial role. KPFM measurement showed that a potential barrier is formed along the GBs and higher SPV is found along the GBs. The c-AFM measurement showed the higher short-circuit current collection near GBs compared with that within grain interior. These two measurements confirm that photogenerated carriers are effectively separated and collected at GBs. Further studies on the composition or different types of vacancies at GBs are required to fully understand how the GBs play these beneficial roles.

**EXPERIMENTAL SECTION**

KPFM and c-AFM measurements were carried out using an AFM (AIST-NT SmartSPM 1000) in air. Nitrogen gun was
used to remove particles on sample surfaces prior to the measurements. Samples were measured immediately after they were removed from nitrogen storage. Both KPFM and c-AFM measurements have shown consistent results for repetitive measurements.

Both c-AFM and KPFM allow for high lateral resolution measurements of spatial variations of the electrical properties of the devices on the nanometre scale. KPFM is a surface potential detection method that determines the CPD during scanning by compensating the electrostatic forces between the probe and the sample. KPFM measurements were performed using a gold-coated Si tip with 6 nm a radius of curvature (HYDRA6R-100NG-10, APPNANO) as the probe in a noncontact mode with an AC voltage of −1 to +1 V.

For c-AFM and KPFM under light illumination, an external tunable laser source with spot size of 9.54 μm² (FemtoPower 1060) was used to irradiated the sample at an angle of ~30° to the surface so the probe does not block the incident light; see Figure 1 for the illustration of the setup. Both wavelength and intensity of the illumination source were controllable. The wavelength of laser light used for the AFM beam deflection was 1300 nm, which is outside the absorption range of the sample under test.

ASSOCIATED CONTENT

Supporting Information

AUTHOR INFORMATION

Corresponding Author
*E-mail: j.yun@unsw.edu.au.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The Australian Centre for Advanced Photovoltaics (ACAP) encompasses the Australian-based activities of the Australia-US Institute for Advanced Photovoltaics (AUSIAPV) and is supported by the Australian Government through the Australian Renewable Energy Agency (ARENA). Responsibility for the views, information or advice expressed herein is not accepted by the Australian Government. J.S. acknowledges support by the Australian Research Council under grant numbers FT110100523, DP140100463, and DP140102849. This work was also supported by the National Research Foundation of Korea funded by the Ministry of Education, Science, and Technology (contract no. NRF-2013S1A2A2035418).

REFERENCES


The Benefit of Grain Boundaries in Organic-Inorganic Halide Planar Perovskite Solar Cells

Jae S. Yun1*, Anita Ho-Baillie1, Shujuan Huang1, Sang H. Woo1, Yoon Heo2, Jan Seidel2, Fuzhi Huang3, Yi-Bing Cheng3, and Martin A. Green1

Jae Sung Yun, Anita Ho-Baillie, Shujuan Huang, Sang H. Woo, Martin A. Green
Australian Centre for Advanced Photovoltaics (ACAP)
School of Photovoltaic and Renewable Energy Engineering
University of New South Wales, Sydney 2052, Australia

Yoon Heo, Jan Seidel
School of Materials Science and Engineering
University of New South Wales, Sydney 2052, Australia

Fuzhi Huang, Yi-Bing Cheng
Department of Materials Engineering
Monash University, Victoria 3800, Australia

Corresponding Author

Name: Jae Sung Yun

Address: Australian Centre for Advanced Photovoltaics (ACAP) School of Photovoltaic and Renewable Energy Engineering University of New South Wales, Sydney 2052, Australia

E-mail: j.yun@unsw.edu.au
Supporting Information.

A 30 nm thick compact TiO$_2$ layer was deposited onto a clean fluorine doped tin oxide (FTO) coated glass using the spray pyrolysis method as described in ref.\textsuperscript{1} The TiO$_2$ layer was carefully examined to make sure the film is deposited uniformly. Figure S1 illustrates (a) topography and (b) contact potential difference map. As can be seen, round shaped grains sized 50-100 nm are formed and distributed entire surface of the film which is a typical microstructure of spray deposited compact TiO$_2$ layer.\textsuperscript{2} Arithmetic average value of the CPD map is around 14 mV which ensures that the film has fairly uniform work function across the surface of the film.

![Figure S1](image.png)

**Figure S1.** (a) KPFM measurements performed on a TiO$_2$/FTO/glass structure over an area of 3 μm$^2$. (a)Topography map and (b) CPD images taken in the dark.

CH$_3$NH$_3$PbI$_3$ deposition was done on top of the c-TiO$_2$ layer using a gas-assisted method as described in ref.\textsuperscript{3} In brief, 25 μL 45 wt% CH$_3$NH$_3$PbI$_3$ dimethylformamide (DMF) solution was spread on the compact TiO$_2$ coated FTO substrate. Then the solution was spun at 6500 rpm. After 2s a dry argon gas was blown on the solution during the spinning. Finally, the film was annealed at 100 °C for 10 min to remove the residue solvent and induce the crystallization. The gas-assisted method promoted the fast nucleation of CH$_3$NH$_3$PbI$_3$ from DMF solution and the perovskite film (~300 nm) was composed of single-crystal grains with high crystallinity.
Figure S2. (a) Light I-V curves of the Au/CH₃NH₃PbI₃/TiO₂/FTO/glass solar cell. Solar cell with a hole transport layer (HTM) layer is also shown as a reference under AM1.5G illumination. (b) Open circuit voltage ($V_{oc}$) as function of light intensity of Au/CH₃NH₃PbI₃/TiO₂/FTO/glass solar cell.

Figure S3. (a) I-V curves obtained by applying a voltage bias at the AFM tip and (b) $V_{oc}$ as a function of light intensity.

Figure S3 (a) shows I-V curves obtained by applying a voltage bias to the probe tip directly on the vicinity of a GB as a function of light intensity. The tip was positioned directly on a grain boundary where current is relatively high.

$V_{oc}$ in Figure S3 (b) exhibits similar non-linear relationship with light intensity as the $V_{oc}$ of the Au coated device in Figure S2 (b). Note that CPD is a measure of work function difference between the tip and sample. CPD is affected by the electrostatic forces between the probe and the sample so gained values of CPD cannot be directly compared with difference
of LUMO of perovskite and HOMO of TiO$_2$. Therefore, only trend of open circuit potentials are compared.

