Nanoimaging of local photocurrent in hybrid perovskite solar cells via near-field scanning photocurrent microscopy

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ABSTRACT

Photocurrent generation of methylammonium lead iodide (CH₃NH₃PbI₃) hybrid perovskite solar cells is observed at the nanoscale using near-field scanning photocurrent microscopy (NSPM). We examine how the spatial map of photocurrent at individual grains or grain boundaries is affected either by sample post-annealing temperature or by extended light illumination. For NSPM measurements, we use a tapered fiber with an output opening of 200 nm in the Cr/Au cladded metal coating attached to a tuning fork-based atomic force microscopy (AFM) probe. Increased photocurrent is observed at grain boundaries of perovskite solar cells annealed at moderate temperature (100 °C); however, the opposite spatial pattern (i.e., increased photocurrent generation at grain interiors) is observed in samples annealed at higher temperature (130 °C). Combining NSPM results with other macro-/microscale characterization techniques including electron microscopy, x-ray diffraction, and other electrical property measurements, we suggest that such spatial patterns are caused by material inhomogeneity, dynamics of lead iodide segregation, and defect passivation. Finally, we discuss the degradation mechanism of perovskite solar cells under extended light illumination, which is related to further segregation of lead iodide.

Keywords: Perovskite, grain boundaries passivation, near-field scanning optical microscopy (NSOM), near-field scanning photocurrent microscopy (NSPM), nanoscale measurement, lead iodide, light-induced degradation, degradation mechanism

1. INTRODUCTION

Finding ways to make cost-effective photovoltaics (PVs) is one of the most significant tasks to address current societal issues, such as the greenhouse effect, air pollution, exhaustion of traditional energy sources, etc. Tandem photovoltaics have been intensively investigated in order to achieve high power conversion efficiency [1], [2]. However, such cells are still costly and limited by materials selection. Also, they require complicated fabrication processes preventing their commercialization as cost-effective energy sources. Nanophotonic engineering has also been extensively studied to increase cost-effectiveness of photovoltaics. High power conversion efficiencies have been observed with low-cost, environmentally-friendly, and earth-abundant nano-materials (e.g., micro-/nanosize cellulose fibers, nanosize glass beads, etc.), with reported improvement of more than 20% over bare cells [3]-[6]. However, more studies of durability (both mechanical and environmental) are still needed to fully commercialize such approaches [7].

Perovskite solar cells have attracted significant interest in the PV research community due to their easy fabrication process, low-cost, and the surprisingly fast progress of power conversion efficiency. Currently, the efficiency of the best perovskite solar cell is comparable to that of traditional multi-crystalline semiconductor-based PVs (e.g., cadmium telluride, silicon, etc.) [8], [9]. However, perovskite solar cells also have multiple instability (e.g., degradation, hysteresis, etc.) issues driven by several environmental factors, such as light illumination, humidity, temperature, etc. Such issues have impeded the broad deployment of perovskite solar cells as commercial PVs. Therefore, the origin of the instability should be further examined. Other unknown factors contributing to the degradation should be identified, and potentially hazardous side-effect should also be addressed as this technology involves toxic materials (e.g., lead).

Multiple characterization techniques have been applied to understand in-depth compositional/structural properties and

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operational principles of perovskite solar cells [10]–[12]. However, to fully understand the operational principles and/or the causes of the aforementioned instability, detailed studies should be made at the nanoscale, where photo-excited carrier generation and collection actually take place.

In this work, we investigate photocurrent generation and collection of perovskite solar cells at the nanoscale using a near-field scanning photocurrent microscopy (NSPM) technique. We observe opposite carrier collection spatial patterns related to the post-annealing temperature of samples. The nanoscale measurement is correlated with other macro-/micro characterization techniques, such as x-ray diffraction, electron microscopy, current density-voltage measurement, etc. Based on the combined characterizations, we attribute the different nanoscale behavior to the dynamics of lead iodide (PbI2) segregation and defect passivation. Finally, we also discuss how an extended light illumination causing the cell degradation affects the microstructure and the local carrier collection.

2. RESULTS AND DISCUSSION

We fabricate perovskite solar cells and characterize their properties at the macro- and nanoscale. We employ a two-step spin-coating method to deposit methylammonium lead iodide perovskite layer (CH3NH3PbI3, MAPbI3 hereafter) on a hole transport layer made from nickel oxide (NiOx). The hole transport layer is coated on an indium tin oxide (ITO) substrate. An electron transport layer is made from [6,6]-phenyl C61 butyric acid methyl ester (PCBM), and a 120 nm thick silver (Ag) contact is formed atop the PCBM layer for carrier extraction. The cross-sectional scanning electron microscopy (SEM) image of the fabricated sample is shown in Fig. 1a.

![Cross-sectional SEM image showing the structure of the fabricated perovskite solar cell. Scale bar is 250 nm.](image1)

![Cross-sectional SEM images showing the perovskite layers annealed at 100 °C (top) and 130 °C (bottom), respectively. Scale bars are 250 nm.](image2)

![X-ray diffraction patterns (#: PbI2, *: MAPbI3) and current density-voltage curves for samples annealed at 100 °C (blue) and 130 °C (red), respectively.](image3)

Figure 1. (a) A cross-sectional SEM image showing the structure of the fabricated perovskite solar cell. Scale bar is 250 nm. (b) Cross-sectional SEM images showing the perovskite layers annealed at 100 °C (top) and 130 °C (bottom), respectively. Scale bars are 250 nm. (c) X-ray diffraction patterns (#: PbI2, *: MAPbI3) and (d) current density-voltage curves for samples annealed at 100 °C (blue) and 130 °C (red), respectively.
We applied two different post-annealing temperatures, 100 °C and 130 °C, to form crystalline structures. Depending on the annealing temperature, we observe different microstructure of lead iodide (PbI₂) within the samples (see SEM images in Fig. 1b). In the sample annealed at higher temperature (130 °C), we find distinct and bright spots at grain boundaries (see spots marked with yellow dotted circles). They can be identified as PbI₂ crystallites due to their low conductivity and the accumulation of electrons during SEM imaging processes. However, the distribution of PbI₂ is relatively uniform across the sample that is annealed at moderate temperature (100 °C) and no significant PbI₂ crystallites are found.

Despite the different distribution of PbI₂ crystallites, both samples have similar intensities of PbI₂ lines in x-ray diffraction patterns (see Fig. 1c). The intensities of perovskite (i.e., MAPbI₃) lines are also similar. Current density-voltage (J-V) characteristics show both higher current density and voltage in the sample annealed at 100 °C (see Fig. 1d). This corresponds to 14.65 % higher power conversion efficiency for this sample (16.98 % vs. 14.81 %). Repeated measurements under identical conditions yield maximum variation of less than 1 % [13].

Figure 2. (a) A picture showing the NSPM probe. (b) A schematic describing the NSPM measurement technique. (c) Time dependent environmental factors (temperature and relative humidity) inside the AFM chamber when NSPM measurements are performed. (d) Line scan profiles of NSPM measurements near the Ag electrode of the sample.

To shed light on the role of the post-annealing, we investigate photovoltaic operation at the nanoscale where photo-excited carrier generation and collection take place. We employ a near-field scanning photocurrent microscopy technique to image photocurrent. In this measurement, a tuning fork-based non-contact mode atomic force microscopy (AFM) probe is used. A multimode optical fiber is attached to the probe to locally illuminate the samples [13]–[15]. The end of the optical fiber is coated with metal (20 nm of Cr and 200 nm of Au) and has ≈ 200 nm output hole for photon injection (see Fig. 2a). The other end of the optical fiber is connected to a bench top diode laser (a wavelength of 635 nm
or 780 nm) via a FC/PC connector. The NSPM probe has a spring constant of 15 N/m at a resonance frequency of ≈ 35 kHz.

For NSPM measurements, perovskite solar cells are placed onto a piezo stage within an AFM system. As the NSPM probe makes a raster scanning, topography and photocurrent signals are obtained at the same time (see Fig. 2b). To amplify the detected signals, a variable-gain low-noise amplifier is used with a gain of $10^7$ A/V, and the amplified photocurrent is then detected by a lock-in technique. We keep the distance between the NSPM probe and the top surface of the perovskite solar cell at ≈ 10 nm during the measurements.

![NSPM images](image)

**Figure 3.** (a) NSPM images on the first set of samples annealed at 100 °C and 130 °C. Measurements are performed at a wavelength of 635 nm. (b) NSPM images on the second set of samples annealed at 100 °C and 130 °C. Measurements are performed at two different wavelengths: 635 nm and 780 nm. Scale bars are 500 nm.

During all measurements, environmental factors within the AFM chamber that can affect the cell operation (e.g., relative humidity and temperature) are accurately controlled (see Fig. 2c). NSPM measurements are performed near Ag contacts to increase signal to noise ratio (SNR). To find measurement areas that offer maximum SNRs, we first perform line
scans near the boundary between the Ag contacts and the PCBM layer. NSPM measurements are then carried out at the areas of maximal signal (see Fig. 2d). While performing NSPM measurements, laser power is optimized to maintain high enough SNR while avoiding sample degradation. Three repeated line scan profiles in Fig. 2d confirm no undesired light-induced sample degradation during the NSPM measurements.

A clear spatial pattern contrast is observed in NSPM images of samples annealed at two different temperatures (see results for first set of samples in Fig. 3a). Measurements are performed at a wavelength of 635 nm where the sun spectral irradiance is near maximum. In the sample annealed at 100 °C, higher photocurrent is generated and collected at grain boundaries. Meanwhile, the opposite spatial pattern is observed in the sample annealed at 130 °C: higher photocurrent at grain interiors and lower photocurrent at grain boundaries. Note that the photocurrent contrast is not caused by the thickness variation. Significant variation of photocurrent (more than 20 %) is observed with a limited height variation (≈ 10 nm) corresponding to less than 2.5 % variation in the absorber thickness. The increased photocurrent collection at grain boundaries of the sample annealed at 100 °C can be explained by the beneficial role of PbI$_2$ passivation [13], [16]. As the annealing temperature increases to 130 °C, however, more structural and functional changes from MAPbI$_3$ to PbI$_2$ takes place, forming distinguishable PbI$_2$ crystallites at grain boundaries, as confirmed by the SEM image in Fig. 1b. The segregated PbI$_2$ phase leads to an increased carrier recombination at grain boundaries, and therefore grain boundaries become less efficient carrier collectors for this sample. NSPM measurements of another set of samples at two different wavelengths: 635 nm and 780 nm (see Fig. 3b) confirm such behavior. Measurements at a wavelength 780 nm are additionally performed to observe the nanoscale photo-excited carrier generation and collection near the bandgap of the active material (i.e., perovskite) with light penetrating deeper in the absorber.

We also conduct NSPM measurements to understand the mechanism behind the instability and degradation of perovskite solar cells under normal light illumination. NSPM measurements are conducted in the multiple stages of the light-induced degradation process under extended light illumination (AM1.5G 0.1 sun, ≈ 25 % relative humidity in air at room temperature). We find that the degradation patterns under continuous light illumination proceed in different ways in two different samples. In the sample annealed at 100 °C, we observe suppressed carrier collection at some grain boundaries. More structural and compositional transformation from MAPbI$_3$ to PbI$_2$ occurs under the continuous light illumination, and the positive role of lead iodide passivation at such grain boundaries fades away. This seriously affects the overall performance of this sample, leading to rapid degradation of the photovoltaic properties under an extended light illumination. However, grain interiors remain the dominant carrier collection paths for the sample annealed at 130 °C regardless of the light illumination time. This results in a more robust behavior of this sample under an extended light illumination. In summary, the sample annealed at 130 °C is more robust under extended light illumination, and such behavior is closely related to the segregation of PbI$_2$ crystallites at grain boundaries.

3. CONCLUSIONS

We investigate nanoscale photo-excited carrier generation and collection of methylammonium lead iodide perovskite solar cells. Combining the results from nanoscale NSPM photocurrent measurements with other characterization techniques, we reveal the carrier dynamics, the role of lead iodide, the effect of sample preparation temperatures at the macro-/nanoscale. Enhanced photo-excited carrier collection is observed at grain boundaries in the sample annealed at 100 °C, while significantly higher photocurrent is measured at grain interiors in the sample annealed at 130 °C. Such spatial patterns are related to the material inhomogeneity and the dynamics of lead iodide segregation. We also suggest the degradation mechanism of perovskite solar cells under extended light illumination based on the results from NSPM measurements. The structural and compositional changes in perovskite layer under extended light illumination suppress the beneficial role of grain boundaries in the sample annealed at 100 °C.

ACKNOWLEDGEMENTS

D. Ha and Y. Yoon acknowledge support under the Cooperative Research Agreement between the University of Maryland and the Center for Nanoscale Science and Technology at the National Institute of Standards and Technology, Award 70NANB14H209, through the University of Maryland.
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