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Photoconductive noise microscopy revealing quantitative effect of localized electronic traps on the perovskite-based solar cell performance

Duckhyung Cho, Taehyun Hwang, Dong-guk Cho, Byungwoo Park, Seunghun Hong

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**ABSTRACT**

We developed a “photoconductive noise microscopy” method to directly image electronic charge traps distributed on a methylammonium lead iodide perovskite film in a solar cell device. The method enabled quantitative imaging of trap densities along with local photocurrents on the solar cell film. By analyzing the imaging data, we could reveal quantitative correlations between the trap distribution and local photocurrents. The results show that the spatial density of the charge traps has a power-law relationship with the short-circuit currents during a solar cell operation as well as localized photocurrents under a sample bias, indicating that a charge trap distribution in a perovskite film can be a major factor determining the performance of the perovskite-based solar cells.

1. Introduction

Organic-inorganic hybrid perovskite materials have recently attracted significant interests due to their superb light-harvesting characteristics [1–9]. Over past few years, extensive efforts have been devoted to develop high-performance photovoltaic devices based on the perovskite materials, resulting in a remarkable solar cell power conversion efficiency over 20% [8]. The perovskite thin films used for the solar cell applications are typically polycrystalline ones, comprising microstructures such as grains and grain boundaries [10,11]. Therefore, the microscopic investigation and engineering of the perovskite films should be essential for the further improvement of the perovskite devices. Some pioneering researches have been performed recently to study the photoresponse properties of perovskite films at a microstructural level [10–13]. One of the remarkable observations in the works is that the photoresponse properties can have significant local variations even in the same perovskite film [10,12,14]. For example, the grain structures in perovskite films showed a rather large variation in the contact potential difference measurements [14]. Also, a polycrystalline perovskite film exhibited substantial grain-to-grain variations in its local photocurrents and short-circuit currents, which can significantly affect the overall performance of a solar cell device based on the film [10,12]. However, it is still unclear about the nanostructural origin of such local variations in the solar cell performance.

Herein, we developed a “photoconductive noise microscopy” method to quantitatively image localized electronic traps generating electrical noises in a photoconductive film. Then, we used the method to investigate a methylammonium lead iodide (CH3NH3PbI3) perovskite film-based solar cell, revealing that the traps in the perovskite film can be a major factor determining the local performance of the solar cell. In this method, we mapped grain-by-grain localized electrical currents and noises on a perovskite film-based solar cell using a nanoscale conducting probe under different light conditions. Then, the maps of currents and noises were analyzed to obtain the distribution of localized photocurrents and trap densities in the solar cell film directly. We observed a large grain-by-grain variation of the local photocurrents and trap densities in the solar cell film. Importantly, the trap densities in the perovskite film were found to have power-law relationships with the local photocurrents and short-circuit currents, while the distribution of local dark currents and short-circuit currents showed no significant correlation. The results imply the traps play a significant role in the recombination of photogenerated carriers in a perovskite film, thus determining the performance of perovskite-based solar cells. Our results provide a valuable insight on the operation of perovskite-based solar cell and an important guideline to improve its performance further.

2. Experimental

2.1. Photocurrent and noise mapping

A Pt-based conducting probe (25Pt300B, Park Systems) installed on an AFM (XE-70, Park Systems) was approached and contacted to the
The as-deposited perovskite layer was sintered at 500 °C for 30 min. The CH$_3$NH$_3$PbI$_3$ crystal structure was examined by x-ray diffraction (D8 Advance: Bruker), and the field-emission scanning electron microscope (Merlin Compact: Zeiss) was used to observe the surface and cross-sectional morphology.

### 3. Results and discussion

Fig. 1a is the schematic diagram showing our experimental setup for the imaging of charge traps and local photocurrents on a CH$_3$NH$_3$PbI$_3$ perovskite film-based solar cell. The details about the solar cell fabrication and photoconductive noise microscopy set-up are described in the method section. In brief, the CH$_3$NH$_3$PbI$_3$ perovskite film of ~400 nm thickness was prepared on a compact TiO$_2$ layer on a fluorine doped tin oxide (FTO)-coated glass via a solution-based antisolvent strategy [15-17]. Thus, a CH$_3$NH$_3$PbI$_3$/TiO$_2$ heterojunction solar cell structure was formed, and the CH$_3$NH$_3$PbI$_3$ layer acted as a photo-reactive layer as well as a hole conducting layer [14,18,19]. The FTO layer worked as an electron-collecting electrode, and the TiO$_2$ layer on the FTO film acted as a hole blocking layer [18]. Then, a Pt-based conducting probe installed on a conductive atomic force microscopy (cAFM) was contacted to the perovskite film and used as a nanosize hole-collecting electrode. Further, we combined a power-adjustable light source with the AFM, for photoconductive noise microscopy measurements [20,21]. While operating the solar cell film with light illumination and a bias voltage, the current signals through the probe were measured and amplified by a preamplifier connected to the probe. The measured current can show the local current generation of the solar cell film at the location of the probe. Simultaneously, a noise component in the localized current was measured using a home-built noise spectrum analyzer comprising a band-pass filter and a RMS-to-DC converter [22]. By scanning the probe over the sample area, we were able to obtain the maps of the localized photocurrents and current noises. The measured noise map was analyzed to calculate the distribution of charge traps. By comparing the current and noise maps measured under the dark and illuminated conditions, we could obtain the maps showing the distribution of local photocurrents and current noise changes in the solar cell film.

Fig. 1b is the energy-level diagram of a CH$_3$NH$_3$PbI$_3$/TiO$_2$ heterojunction solar cell structure. The diagram shows the conduction-band minimum (CBM) and the valence-band maximum (VBM) of CH$_3$NH$_3$PbI$_3$ and TiO$_2$. When the CH$_3$NH$_3$PbI$_3$ layer absorbs light, valence electrons are excited into the conduction band, leaving holes in the valence band. The excited electrons at the CBM of the CH$_3$NH$_3$PbI$_3$ (−3.93 eV vs. vacuum) pass into the TiO$_2$ layer which has a lower CBM (−4.10 eV) compared to the CH$_3$NH$_3$PbI$_3$. The holes at the VBM of the surface of the CH$_3$NH$_3$PbI$_3$ film as described in the Fig. 1a. Here, the contact force of the AFM probe to the film surface was maintained as 2 μN via the contact force feedback loop of the AFM system. A dc bias voltage was applied between the AFM probe and the FTO substrate using a function generator (DS345, Stanford Research Systems), and current signals through the probe were measured and amplified by a low-noise preamplifier (SR570, Stanford Research Systems) connected to the probe as described in the Fig. 1a. The amplified current signals were filtered by a band-pass filter included in the preamplifier to obtain the electrical noise signal which is the fluctuating component of the current signals. The RMS power of the noise signal could be obtained using a RMS-to-DC converter built using an AD737 chip (purchased from Analog Devices). Note that the obtained noise power is the integrated value of the noise PSDs over the frequency range of the pass band of the used band-pass filter. Finally, we get the noise PSD value at the central frequency of the pass band, by dividing the measured noise power with the bandwidth of the band-pass filter. By scanning the AFM probe while measuring both current and noise PSD on the CH$_3$NH$_3$PbI$_3$ film surface, we could obtain the current and noise PSD maps simultaneously. Further, we measured a current map while illuminating a white light to the film using a light source (LS-F100HS) and compared the map with that obtained at a dark condition to obtain a photocurrent map.

### 2.2. TiO$_2$ layer on FTO substrate

TiO$_2$ precursors of 150 mM and 300 mM titanium diisopropoxide bis(acetylacetone) solutions (in 1-butanol) were prepared. Then, 150 mM precursor was spin-coated at 2500 rpm on FTO substrate followed by 125 °C for 20 min drying. Additional spin-coating was performed identical to above using 300 mM precursor, and the substrate was finally sintered at 500 °C for 30 min.

### 2.3. CH$_3$NH$_3$PbI$_3$ deposition and material characterization

CH$_3$NH$_3$PbI$_3$ precursor solution was prepared by mixing stoichiometric CH$_3$NH$_3$I (1.2 M) and PbI$_2$ (1.2 M) in n,n-dimethylformamide at room temperature. The perovskite precursor was dropped on the TiO$_2$-coated FTO substrate, and spin-coating was done at 5000 rpm for 20 s. The antisolvent strategy using toluene for fast crystallization was utilized. The as-deposited perovskite film was then annealed at 120 °C for 50 min. The CH$_3$NH$_3$PbI$_3$ crystal structure was examined by x-ray diffraction (D8 Advance: Bruker), and the field-emission scanning electron microscope (Merlin Compact: Zeiss) was used to observe the surface and cross-sectional morphology.
CH3NH3PbI3 are injected into the Pt-based conducting AFM probe. The TiO2 layer and the bottom FTO substrate act as a hole-blocking layer and an electron collector, respectively. Such CH3NH3PbI3/TiO2 heterojunction structure with FTO and metal contacts has been reported to be very efficient in harvesting light energies, and also is useful in studying the basic characteristics of CH3NH3PbI3 due to its simple structure without an additional hole-transport layer [14,18,19].

The scanning electron microscopy (SEM) image in Fig. 2a shows well-defined interfaces between CH3NH3PbI3 and the compact TiO2 layer with the uniform thickness of perovskite, demonstrating the high quality of the heterojunction solar cell film. Also, Fig. 2b shows the x-ray diffraction (XRD) spectroscopy results of the CH3NH3PbI3 film. The data show a strong CH3NH3PbI3 (110) peak and the negligible residual PbI2, indicating the purity of the CH3NH3PbI3 film.

Fig. 2c shows the current-voltage curves of the solar cell film measured with (red line) and without (blue line) the illumination of a white light with its power density of 100 mW/cm². Here, we measured electrical currents (I) through the CH3NH3PbI3/TiO2 between the conducting probe at a bias voltage (V) and the electrically-grounded FTO substrate. In the dark condition, a typical asymmetric I-V curve of a p-n junction was observed. When the film was illuminated with the light, the current level was increased significantly compared to the dark condition, indicating the significant generation of photocarriers in the CH3NH3PbI3 film. In addition, a short-circuit photocurrent of ~ 1 nA was observed at the zero-bias condition, indicating the successful collection of the photocarriers in our CH3NH3PbI3/TiO2 heterojunction solar cell structure with the Pt probe. Fig. S1 shows the structure of a solar cell device based on the CH3NH3PbI3 film and a current density-voltage curve of the device under a light with its intensity of 100 mW/cm². The measured efficiency of the cell was ~ 13%, demonstrating the solar cell film could be used as an efficient light harvester.

Fig. 3a shows an AFM topography image of a CH3NH3PbI3 film on a TiO2/FTO layer in the solar cell structure. The contact force of the conducting AFM probe to the film surface was maintained as 2 μN during the AFM scanning. The topography image shows that the CH3NH3PbI3 film consisted of adjoined small CH3NH3PbI3 grains. The sizes of individual grains varied between 500 and 1000 nm laterally in their diameters, which are as large as the film thickness. The SEM image in Fig. 2a clearly shows that individual grains extended throughout the film in a vertical direction without any grain boundaries, which is also
consistent with previous reports [14,23].

A localized current map in a dark condition was measured simultaneously with the topography image (Fig. 3b). To measure the dark current map, a DC bias voltage of 1.6 V was applied to the conducting probe, and the FTO substrate was electrically grounded. Then, the current through the AFM probe was recorded while the probe scanned over the film surface to obtain the current map. The result shows that the overall region of the CH$_3$NH$_3$PbI$_3$ film was conductive, and the average current level was ~ 1.8 pA under the dark condition. The boundaries of CH$_3$NH$_3$PbI$_3$ grains identified in the topography map exhibited rather high current levels compared with the interior regions of individual grains, which could be attributed to the thinner film thickness near the grain boundaries. The localized current could be successfully mapped for the whole scanned area, indicating that the conducting AFM probe and the film surface made a stable electrical contact regardless of the topological roughness of the film, which should be essential for the reliable current and noise measurements.

Since the resistance of the CH$_3$NH$_3$PbI$_3$ film is much higher than that of the FTO, we can assume that charge carriers mainly flowed in a vertical direction from the underlying FTO substrate to the AFM probe passing through the perovskite layer [14,24,25]. In such a case, currents flowing in the lateral direction along the film surface are negligible, and various noise sources inside or on the perovskite film can be responsible for the measured noises [14,24,25].

The current-normalized noise power spectral density ($S_f/I^2$) value can be a useful parameter to represent the electrical-noise level of an electronic channel [24]. Fig. 3c shows the map of $S_f/I^2$ (at 170 Hz) estimated from the noise power spectral density (PSD) map measured simultaneously with the current map under a dark condition. Here, we first measured the noise PSD ($S_f$) at 170 Hz via the noise microscopy, and divided the measured $S_f$ map by the square of the current map to obtain the $S_f/I^2$ map. Note that the $S_f/I^2$ level varied significantly between grains, while it did not vary much inside each individual grain. For example, a grain marked with (i) in the Fig. 3c showed the $S_f/I^2$ value of ~ 3 × 10$^{-8}$ Hz$^{-1}$ which is ~ 40 times higher than the $S_f/I^2$ value of ~ 7 × 10$^{-8}$ Hz$^{-1}$ in the grain marked with (ii). Interestingly, the dark current map (Fig. 3b) and the noise map (Fig. 3c) do not show any correlations, implying that the noise sources in the CH$_3$NH$_3$PbI$_3$ film did not affect its dark conductivity. This is a noteworthy observation considering that noise sources in many of the electronic materials seriously degrade their conductivity [24]. Previously, it was suggested that the charge-carrier scattering in a polycrystalline perovskite film is dominated by the lattice scattering (phonon scattering), while the main carrier scattering mechanism in many other amorphous electronic materials can be the impurity scattering [26]. In the case of the lattice scattering, impurities like deep levels or charge traps, which often work as noise sources, might not much degrade the carrier mobility or the conductivity, which is consistent with our observation [26].

Fig. 3d shows $S_f$ and $S_f/I^2$ (at 170 Hz) measured in a grain marked by (i) in Fig. 3c with different bias voltages under the dark condition. Note that the $S_f$ values increased as the bias-voltage increased. However, the $S_f/I^2$ values were nearly constant regardless of the applied voltage. It was previously reported that the main intrinsic source of low-frequency noise in perovskite films is charge traps generating carrier-number fluctuations [27-29] and the measured $S_f/I^2$ values in a conducting channel can be utilized to estimate the concentration of such noise sources [24,27]. Our observation indicates the measured $S_f/I^2$ values measured in our solar cell film are not much affected by external bias voltages and thus can be used to estimate the noise source densities representing the intrinsic properties of the film.

Fig. 3e shows the $S_f/I^2$ spectra which were measured at two different locations on the film. Here, the probe (biased at 1.6 V) was in contact with a specific position on the CH$_3$NH$_3$PbI$_3$ film, and the electrical currents through the conducting AFM probe were measured and analyzed using a fast Fourier transform (FFT) signal analyzer (SR770, Stanford Research Systems). The noise PSD versus frequency ($f$) spectra measured at locations indicated by (i) and (ii) in Fig. 3c were represented by red and blue symbols, respectively. The slopes of the both curves were close to ~ 1, indicating 1/f noise behaviors of the CH$_3$NH$_3$PbI$_3$ film. Those behaviors are consistent with the known 1/f noise behavior of a polycrystalline perovskite film [30]. In our previous works about electrical noises using nanoscale probes, we showed that when the electrical noises were mainly generated by a small number of noise sources in the nanoscale tip-substrate contact area on the substrate surface, the frequency spectra of the noise PSDs exhibited a 1/f$^2$ behavior [31-33]. And, the behavior was attributed to rather uniform characteristic trapping times of such a small number of noise sources in the nanoscale contact regions. On the other hand, when electrical noises were generated by a rather large number of noise sources with a rather large variation of characteristic trapping times, we observed a 1/f behavior [31-33]. The 1/f behavior in our result indicates that the electrical noises were mainly generated by a rather large number of noise sources inside the perovskite films.

We developed a method to quantitatively estimate the density of localized charge traps in a perovskite film using the measured $S_f/I^2$ map. In this method, we assumed that the measured 1/f noises in the perovskite-based solar cell junction were generated by the carrier-number fluctuation in the perovskite film layer, as suggested by a previous report [30]. Because the capture and release of charge carriers by a trap are random processes, the number of traps occupied by the carrier fluctuates randomly with time, generating electrical noises [32,33]. At a dark condition, the perovskite layer has a much higher resistivity than the TiO$_2$ layer [34,35]. In addition, at a high forward bias condition, the voltage drop at the diode contact between the perovskite/TiO$_2$ junction should be much smaller than that at the highly-resistive perovskite layer. Thus, we could assume that the most of voltage drops occurred at the perovskite layer in our solar cell structure at a dark condition with a high forward bias voltage. Then, let’s consider a conducting AFM probe in contact with a CH$_3$NH$_3$PbI$_3$ perovskite film surface at a position of ($x$, $y$) on the film surface. The noise PSD of the number of occupied traps ($S_{\text{nt}}$) in the small CH$_3$NH$_3$PbI$_3$ film segment in contact with the probe can be written like [32,36,37],

$$
S_{nt}(f, x, y) = \Delta x \Delta y \sum_{E} \int \frac{4\pi E_f (x, y, z)}{1 + [2\pi f_0^{-1} E_f (x, y, z)]^2} f_f (1-f_f) \cdot N(E_f, x, y, z) dz dE \tag{1}
$$

where the $N_e$, $f_f$, $f_f$, and $r$ are the density of traps over space and energy, the trap occupancy function, a frequency, and a trapping time constant, respectively. The integration in the z direction (vertical direction to the film surface) ranges from 0 to the thickness of the CH$_3$NH$_3$PbI$_3$ film. At room temperature, $f_f (1-f_f)$ behaves like a delta function around the Fermi level, and Eq. (1) after the integration over electron energy $E$ can be written as [38]

$$
S_{nt}(f, x, y) = \Delta x \Delta y kT \sum_{E} \int \frac{4\pi E_f (x, y, z)}{1 + [2\pi f_0^{-1} E_f (x, y, z)]^2} N(E_f, x, y, z) dz \tag{2}
$$

Here, we define the effective trap density $N_{\text{eff}}$ like

$$
N_{\text{eff}}(f, x, y) \equiv \int \frac{4\pi E_f (x, y, z)}{1 + [2\pi f_0^{-1} E_f (x, y, z)]^2} N(E_f, x, y, z) dz \tag{3}
$$

Then, Eq. (2) can be simply rewritten as

$$
S_{nt}(f, x, y) = kT \int N_{\text{eff}}(f, x, y) \cdot \Delta x \Delta y \tag{4}
$$

with the charge carrier number $\Delta C$ in the area $\Delta x \Delta y$ and the electrical current $I$ through the small segment of the CH$_3$NH$_3$PbI$_3$ film, we can write the PSD of the current noises generated by the segment as [32]...
\[ S_f(x, y) = \frac{(I_f)^2}{(\Delta C)^2} \int S_x(x, y) = \frac{(I_f)^2}{(\Delta C)^2} \frac{kT}{f} N_{\text{eff}}(x, y) \Delta x \Delta y \]  

(5)

Then, \( N_{\text{eff}} \) can be written as

\[ N_{\text{eff}}(x, y) = \frac{(\Delta C)^2}{(I_f)^2} \int f S_f(x, y) \frac{kT}{\Delta x \Delta y} \]  

(6)

It is worth discussing a few interesting aspects of the \( N_{\text{eff}} \). First, in the case of \( 1/f \) noise, \( S_f \) at a \((x, y)\) position is proportional to \( 1/f \). Thus, \( S_f \times f \) is constant at a position \((x, y)\), and \( N_{\text{eff}}(x, y) \) can be expressed as \( N_{\text{eff}} \). Furthermore, considering that the \( N_{\text{eff}} \) is the integrated value of the trap density over the \( z \)-direction, it can be a convenient value to represent the effective number of charge traps per unit area in a two-dimensional film.

Utilizing Eq. (6), we calculated the map of the effective trap density \( N_{\text{eff}} \) from the \( S_f/F \) map in Fig. 3c (Fig. 3f). For the calculation, we used the \( \Delta x \Delta y \) value of \( \sim 100 \) nm\(^2\) which is the effective contact area of our conducting AFM probe provided by the manufacturer. For \( \Delta C \), we used a reported value \((\sim 10^{18} \) cm\(^{-3}\)) of carrier concentrations in a CH\(_3\)NH\(_2\)PbI\(_3\) film [39]. The calculated \( N_{\text{eff}} \) map shows the non-uniform distribution of traps over the film (Fig. 3f). The \( N_{\text{eff}} \) inside individual grains ranges from \( 10^{15} \) to \( 10^{16} \) cm\(^{-2}\) \( \text{eV}^{-1}\). In the grain boundary regions, the trap density was distinctly high reaching \( \sim 10^{17} \) cm\(^{-2}\) \( \text{eV}^{-1}\), presumably due to the disordered nature of the boundary regions. The charge trap distribution has been believed to significantly affect the photovoltaic characteristics of a photoreactive film, and extensive research efforts have been devoted to study such traps [40]. However, until now, it has been very difficult, if not impossible, to image the nanoscale distribution of charge traps in a photoreactive film. Thus, our results should be a significant breakthrough in the research on a perovskite film and show the versatility of our noise mapping method. It is also worth mentioning the possible applications and limitations of our method. Since our method can be applied to various conducting substrates, as long as a nanoscale conducting probe can make a good electrical contact on their surfaces, it can be applied to diverse optoelectronic devices based on various materials such as conducting polymers and graphene [24,31,33]. However, for some conducting materials with a rather thick surface oxide layer under ambient conditions, the measurement may have to be done under vacuum environments.

To further study the effect of the charge trap distribution on the local photovoltaic characteristics of the CH\(_3\)NH\(_2\)PbI\(_3\) film, we imaged a rather large area of the film under different illumination and bias conditions (Fig. 4). Fig. 4a, b show topography and dark current maps measured over a 15 \( \times \) 15 \( \mu \)m\(^2\) region of the CH\(_3\)NH\(_2\)PbI\(_3\) film. The topography map shows more than a hundred of different topological grains in the region. The dark current map was measured under the dark condition with a DC bias voltage of 1.6 V. The dark current level was quite uniform throughout the whole region, and grain boundary regions showed a bit higher dark current level compared to the intragrain regions, presumably due to the thinner film thickness at the grain boundaries. Fig. 4c shows the photocurrent map in the same region on the perovskite film. Here, a current map was measured at 1.6 V with the light illumination of 100 mW/cm\(^2\), and it was subtracted by the dark current map (Fig. 4b) to obtain the photocurrent map. The photocurrent map exhibited distinctive grains whose shapes are a bit different from those in the topological image or the dark current map. More than a hundred of grains can be clearly identified with their averaged photocurrent level of \( \sim 7 \) nA. Interestingly, the photocurrent level varied significantly between grains in the film, while the dark current in Fig. 4b appeared to be nearly uniform. Fig. 52 shows the photocurrent (at 1.6 V) versus light intensity plot measured at a position marked by a red circle in Fig. 4c. The plot shows the photocurrent was linearly proportional to the light intensity, implying most of light-generated carriers were successfully collected in our calculation setup [41].

Fig. 4d is a scatter plot of the dark current and photocurrent level in individual grains. Here, we utilized an image processing method based on the Sobel algorithm [42] to identify the grain boundary regions where the photocurrent level was abruptly changed in the photocurrent map. Fig. S3 shows the grain-boundary regions (black areas) and individual grains (white areas). Then, the averaged values of dark currents and photocurrents of \( \sim 100 \) identified grains were calculated. Each data point in the Fig. 4d shows the averaged value of dark currents and photocurrents in a single grain identified in the Fig. S3. In the plot, we could not observe a significant correlation between the dark current and the photocurrent, which clearly shows that the photococonductance of a perovskite film has no direct relation with its dark resistivity. Previously, it was suggested that the photococonductance in perovskite films could be significantly affected by various nanostructures such as charge traps in them [3,40,43]. On the other hand, their resistivity under a dark condition is suggested to be mainly determined by the lattice structures of the film rather than the traps, which is consistent with our results [26].

Fig. 4e shows the effective trap density \( N_{\text{eff}} \) obtained from a \( S_f/F \) map (at 170 Hz) measured simultaneously with the dark current map in Fig. 4b. Note that the grains with a high trap density \( N_{\text{eff}} \) in Fig. 4e exhibited a rather low photocurrent level in Fig. 4c. This result clearly shows that the charge traps can degrade the photococonductance in a perovskite film.

Fig. 4f shows a scatter plot showing the relation between the trap density and photocurrent level of grains in the CH\(_3\)NH\(_2\)PbI\(_3\) film. Each data point shows the averaged photocurrent and trap density values of a single grain identified in the Fig. S3. Here, we can observe a negative correlation between the trap density and the photocurrent level. On the other hand, there was no clear correlation between the trap density and dark current (see Fig. S5). More specifically, the photocurrent level was found to be inversely proportional to the 0.5 power of the trap density. The observation directly shows that the charge trap density \( N_{\text{eff}} \) can be a dominant parameter determining local \( J_{\text{sc}} \) on a perovskite film. One plausible explanation for this result can be a trap-assisted recombination process of photocarriers in a perovskite film [40,44]. When a perovskite film was illuminated with a light, the film can absorb photons to generate electron-hole pairs increasing the number of charge carriers, and the photocurrent \( J_{\text{sc}} \) at a high-forward bias condition should be proportional to the number of generated photocarriers. Previous studies suggested that the traps can assist the recombination of photo-generated electrons/holes and thus reduce the number of photocarriers. In this case, the trap-assisted recombination rate \( r_{\text{recomb}} \) of photocarriers in an illuminated perovskite film can be written like [45]

\[ r_{\text{recomb}} = \frac{C_n C_p N_{\text{eff}}}{(C_n + C_p) N_{\text{eff}}} n \]  

(7)

where \( C_n \) and \( C_p \) are the capture coefficients of traps for electrons and holes, respectively. The \( n \) and \( p \) are the volume density of electrons and the holes including photo-generated ones, respectively. The \( n_0 \) and \( p_0 \) are the electron and hole densities in the dark condition, respectively. In our CH\(_3\)NH\(_2\)PbI\(_3\) film, the photocurrents were 1000 times larger than the dark currents, and thus the total carrier numbers \( p \) and \( n \) under the illumination were much larger than the intrinsic carrier numbers \( p_0 \) and \( n_0 \) under the dark condition. Further, the numbers of photo-generated electrons and holes can be assumed to be identical (as \( n \)), because they are always generated as a pair by absorbed photons. Then, Eq. (7) could be approximated as

\[ r_{\text{recomb}} = \frac{C_n C_p}{(C_n + C_p)} N_{\text{eff}} n \]  

(8)

Here, the \( C_n C_p/(C_n + C_p) \) is a constant which is independent to the \( N_{\text{eff}} \) and \( n \). Previous literatures suggested that \( n \) or \( r_{\text{recomb}} \) is proportional or inversely-proportional to the photocarrier lifetime [46,47]. In this
In this case, we can write like

$$r_{\text{recomb}} \propto \frac{1}{n}$$

(9)

By combining Eqs. (8) and (9), we can expect the correlation between the photocurrent and trap densities like

$$n \propto \frac{1}{(N_{\text{eff}})^{0.5}} \propto I_{\text{pc}}$$

(10)

Eq. (10) suggests that the $n$ as well as the photocurrent $I_{\text{pc}}$ is inversely proportional to 0.5 power of $N_{\text{eff}}$, which is consistent with our experimental observation in Fig. 4f. Thus, our observation on the strong $N_{\text{eff}}$-$I_{\text{pc}}$ correlation suggests that the charge traps generating electrical noises can reduce the photocarriers via the trap-assisted recombination mechanism, resulting in the degraded photoconduction of perovskite films [44].

The short-circuit current is an important parameter to estimate the efficiency of a solar cell. Fig. 4g shows a short-circuit current map showing the distribution of local short-circuit current on the perovskite film. With illuminating a white light with a power density of 100 mW/cm$^2$, we mapped the currents with a zero bias voltage. The average level of the short-circuit current was $\sim$ 0.4 nA, which is comparable to a previously-reported value of perovskite-based solar cells [48]. Interestingly, the map showed a large grain-by-grain variation of the short-
In conclusions, we developed a photoconductive noise microscopy method, and applied the method to image the trap distribution and local photocurrents on a CH$_3$NH$_3$PbI$_3$ perovskite film in a solar cell structure. Interestingly, we observed that local photocurrent and trap density varied significantly between individual grains in the film, and the trap density and photocurrent level of a grain had a power-law relationship. These results imply that the charge traps generating the local photocurrents on a CH$_3$NH$_3$PbI$_3$ perovskite film can significantly reduce the solar-cell performance, which can be a key information in designing efficient light-harvesting devices in the future.

4. Conclusions

In conclusions, we developed a photoconductive noise microscopy method, and applied the method to image the trap distribution and local photocurrents on a CH$_3$NH$_3$PbI$_3$ perovskite film in a solar cell structure. Interestingly, we observed that local photocurrent and trap density varied significantly between individual grains in the film, and the trap density and photocurrent level of a grain had a power-law relationship. These results imply that the charge traps generating the local photocurrents in a perovskite film can significantly affect the photocarrier recombination via the trap-assisted recombination mechanism. Furthermore, we observed that the short-circuit current level of a CH$_3$NH$_3$PbI$_3$ grain was inversely proportional to the 0.87 power of the trap density, revealing the trap distribution can be the major factor governing the local performance of perovskite-based solar cells. These results should provide an important guideline in developing more efficient solar cell devices based on the perovskite films.


Dong-guk Cho received his B.S. degree in 2009 in Materials Science from Hanyang University, Korea. In 2011, he received M.S. degree in Materials Science from Hanyang university and is currently a Ph.D. candidate in physics from Seoul national university. His research interests are electrical noises in nanomaterials, fabrication of hybrid nanomaterials, and electrical biosensors.

Byungwoo Park received his B.S. degree in 1981 in Physics from Seoul National University, Korea, M.S. degree in 1984 in Physics from Pennsylvania State University, and Ph.D. degree (1989) in Applied Physics from Harvard University. He worked as a post doctor at IBM T. J. Watson Research Center from 1989 to 1991 and a research fellow at California Institute of Technology from 1991 to 1992. He joined the School of Materials Science and Engineering at Georgia Institute of Technology as an Assistant Professor in 1992. He is currently a Professor in the Department of Materials Science and Engineering at Seoul National University since 1997. His current research interests include the development of nanoscale coating, novel nano-composites, quantum-dot and perovskite solar cells, nanoprobe control of thin-film electrodes, and the growth kinetics of nanostructures.


Duckhyung Cho received his B.S. degree in 2011 in physics from Seoul national university, Korea. In 2013, he received M.S. degree in physics from Seoul national university and is currently a Ph.D. candidate in the physics department at Seoul national university. His research interests are focused on charge transports and noise phenomena in electronic channels.

Taehyun Hwang received his B.S. degree in 2012 in Materials Science and Engineering from Korea Advanced Institute of Science and Technology (KAIST). He is currently a Ph.D. candidate in Materials Science and Engineering at Seoul National University under the supervision of Prof. Byungwoo Park. His current research interests include the fabrication of nanoporous materials, understanding and engineering of microstructural evolution, interface, and optoelectronic properties of organic-inorganic hybrid perovskite for solar cell applications.

Byungwoo Park received his B.S. degree in 1981 in Physics from Seoul National University, Korea, M.S. degree in 1984 in Physics from Pennsylvania State University, and Ph.D. degree (1989) in Applied Physics from Harvard University. He worked as a post doctor at IBM T. J. Watson Research Center from 1989 to 1991 and a research fellow at California Institute of Technology from 1991 to 1992. He joined the School of Materials Science and Engineering at Georgia Institute of Technology as an Assistant Professor in 1992. He is currently a Professor in the Department of Materials Science and Engineering at Seoul National University since 1997. His current research interests include the development of nanoscale coating, novel nano-composites, quantum-dot and perovskite solar cells, nanoprobe control of thin-film electrodes, and the growth kinetics of nanostructures.

Photoconductive noise microscopy revealing quantitative effect of localized electronic traps on the perovskite-based solar cell performance

Duckhyung Cho\textsuperscript{a}, Taehyun Hwang\textsuperscript{b}, Dong-guk Cho\textsuperscript{a}, Byungwoo Park\textsuperscript{b,}\textsuperscript{*}, Seunghun Hong\textsuperscript{a,}\textsuperscript{*}

\textsuperscript{a} Department of Physics and Astronomy, and Institute of Applied Physics, Seoul National University, Seoul 08826, Korea
\textsuperscript{b} Department of Materials Science and Engineering, Seoul National University, Seoul 08826, Korea

\textbf{Fig. S1.} Structure of a CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}-based solar cell device (left) and a current density-voltage curve measured from the device under a light with its intensity of 100 mW/cm\textsuperscript{2} (right). The cell efficiency was \textasciitilde13 \%, showing our solar cell film could be utilized as an efficient light harvester.

\textbf{Fig. S2.} Photocurrent versus light intensity graph measured at a position in a perovskite grain marked by a red circle in Fig. 4c. The bias voltage on the tip was 1.6 V. The photocurrent was increased proportional to the light intensity, implying most of photocarriers were well-collected in our experimental condition.
**Fig. S3.** Grain boundary region (black region) and grains (white islands) computationally identified from the photocurrent map in Fig. 4c.

**Fig. S4.** Scattered plot showing the relation between the effective trap density $N_{\text{eff}}$ and local dark current measured with the noise microscopy images in Fig. 4. There is no significant relation between the $N_{\text{eff}}$ and the dark current.