Supporting Information for

Nanoscale charge accumulation and its effect on carrier dynamics in tri-cation perovskite structures

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Figure S1. (a) Stable photoluminescence (PL) response of CsFAMAPbBrI at 17.5 W/cm². (b) PL peak position against time for different illumination intensities.
Figure S2. Dual-harmonic open-loop KPFM timetraces on CsFAMAPbBrI on ITO. (a) Amplitude of first harmonic signal. (b) Phase of first harmonic signal. (c) Amplitude of second harmonic signal. (d) Calculated contact potential difference. The shown data was recorded at 20 nm lift height at 2 V, 1 kHz off-resonance AC voltage, in dry atmosphere (<1 %RH), using a Pt/Ir coated, 13kHz, ~0.2N/m tip for highest sensitivity. The illumination was done with a 455 nm, ~2.08 mW/cm² intensity laser. The contact potential difference was calculated according to Nanotechnology 24 (2013) 475702.
Figure S3. Mask of grain boundaries prepared from flattened topography map used for separation of $V_{cpd}$ responses in Figure 3.
Figure S4. Pump-probe KPFM response using amplitude modulated pulse waveform. (a) Pump-probe response recorded at $T_{\text{rep}}=20 \, \mu\text{s}$ with the fitted Heaviside function and the exponential time constants. (b) Dependence of extracted time constant against probing duty cycle. The inset shows the variation of the recorded signal at different probing pulse-widths.
Figure S5. Mask of grain boundaries prepared from topography map used for separation of pump-probe KPFM responses in Figure 5.
Figure S6. Imaging of perovskite at ~0.1W/cm² illumination intensity, 633 nm wavelength using PP-KPFM. (a) Topography map (b) "Off" state PP-KPFM image (c) "On" state PP-KPFM image (d) Difference of the two PP-KPFM images.
Figure S7. Local variation of contact potential difference on the perovskite structure. (a) Topography line profile of perovskite/ITO showing clear grain-GB structure. (b) Contact potential difference of a single pixel measured at 12 different lift heights. The $V_{cpd}$ versus tip-sample distance was fitted with a power law as shown in red solid line. (c) Corresponding $V_{cpd}$ profiles recorded at different lift heights. The line profile was extrapolated for 0.1 nm distance using the fit. The clear contrast between grains and GBs shows that it is due to local variation of the $V_{cpd}$, rather than of purely capacitive origin.
Table S1. Extracted time constants and adjusted R2 resulting from $f(x) = y_0 + Ae^{(x/\tau)}$ fit to separate parts of the first harmonic electrostatic response.

|       | S1          | S2          | S3  | S4  | S5  |
|-------|-------------|-------------|-----|-----|-----|
| Step B| $\tau=0.23\pm0.05$ | $\tau=0.10\pm0.04$ | X   | X   | X   |
|       | Adj. $R^2=0.93$ | Adj. $R^2=0.88$ |     |     |     |
| Step C| $\tau=5.94\pm0.23$ | $\tau=-6.31\pm0.14$ | $\tau=1.18\pm0.23$ | $\tau=0.23\pm0.02$ | $\tau=0.86\pm0.05$ |
|       | Adj. $R^2=0.99$ | Adj. $R^2=0.99$ | Adj. $R^2=0.37$ | Adj. $R^2=0.85$ | Adj. $R^2=0.93$ |
| Step E| $\tau=4.24\pm0.20$ | $\tau=3.06\pm0.14$ | $\tau=2.61\pm0.25$ | $\tau=0.81\pm0.06$ | $\tau=2.50\pm0.10$ |
|       | Adj. $R^2=0.97$ | Adj. $R^2=0.96$ | Adj. $R^2=0.65$ | Adj. $R^2=0.93$ | Adj. $R^2=0.98$ |

Supporting Information Note 1.

Open-loop pump-probe Kelvin probe force microscopy and its application

In Kelvin probe force microscopy (KPFM) a sinusoidal electrical signal is applied between the AFM tip and the sample at a fixed frequency which gives rise to an electrostatic force:

$$F_{es} = F_{DC} + F_{\omega} + F_{2\omega}, \quad (1)$$

where $F_{es}$ is the overall electrostatic force, $F_{DC}$, $F_{\omega}$ and $F_{2\omega}$ are the DC, first harmonic and second harmonic components of the total electrostatic force. In KPFM, the first harmonic ($F_{\omega}$) of the electrostatic force is nullified by applying a DC voltage ($V_{DC}$) to the tip or the sample:

$$F_{\omega} = \frac{dc}{dz} V_{AC}\sin\omega t (V_{DC} - V_{CPD}), \quad (2)$$

where $z$ is the tip sample distance, $t$ is time, $C$ is the capacitance, $V_{AC}$ is the applied AC voltage to the tip, $\omega$ is the angular frequency, $V_{DC}$ the applied DC voltage, $V_{CPD}$ is the tip-sample contact potential difference. The contact potential difference can be expressed as:

$$V_{CPD} = \frac{\pm(\Phi_{sample} - \Phi_{tip})}{e}, \quad (3)$$
where $\Phi_{\text{sample}}$ is the work function of the sample, $\Phi_{\text{tip}}$ is the work function of the AFM tip and $e$ is the elementary charge, ‘+’ if the voltage is applied to the sample and ‘−’ if applied to the tip. We note that in our result, we have corrected for the polarity term so that the changes in $V_{\text{CPD}}$ directly correspond to the work function change. Under illumination, induced charge carriers lead to an additional tip-sample potential difference $V_Q$ that will be nullified by the KPFM feedback loop. However, the technique is effectively limited to the sub-millisecond time resolution of the feedback loop. Characterization of faster charge transfer processes can be done by several methods. A pump-probe scanning probe microscopy approach previously described by Hamers et al. consists of well-defined pulse waveforms (a pump and a probing signal) with a continuously changing phase delay that are the sample excitation source and cantilever electrical excitation, respectively. Here, we employed illumination pulsing to generate and characterize electronic charge carriers in the perovskite system. Pulsing the cantilever excitation signal effectively leads to probing the interaction at the “On” state of the pulses. This results in a signal maximum if pump and probe pulses coincide and a minimum if they do not. By phase-shifting the pump and probe signal against each other the temporal response of the charge carrier generation and relaxation can be sampled. According to this scheme the pump signal can be described as:

$$V_{\text{pump}}(t) = \begin{cases} V_0t, & kT_{\text{rep}} \leq t \leq kT_{\text{rep}} + \frac{1}{2}T_{\text{rep}}; \\ 0, & \text{else}, \end{cases} \quad (4)$$

where $V_0$ is the applied pump voltage amplitude to drive the laser, $T_{\text{rep}}$ is the repetition period and $k$ is an integer. The probing signal in this case is:

$$V_{\text{probe}}(t + \tau_{\text{del}}) = \begin{cases} V_{\text{probe}}V_{\text{AC}}\sin\omega_{\text{mod}}t, & (kT_{\text{rep}} + \tau_{\text{del}}) \leq t \leq (kT_{\text{rep}} + \tau_{\text{del}} + \eta_0T_{\text{rep}}); \\ 0, & \text{else}, \end{cases} \quad (5)$$
where $V_{probe}$ is the applied pulse voltage, $\omega_{mod}$ is the angular modulation frequency, $\tau_{del}$ is the time delay between the pump and probe pulses, $k$ is an integer and $\eta_0 = \frac{\tau_{pulse}}{\tau_{rep}}$ is the duty cycle of the probe signal. With a $t_s$ sampling time, this results in integration over $\frac{t_s}{\tau_{rep}}$ number of periods of the electrostatic force response of the tip-sample system. Every recorded data point with $t_s$ spacing is going to be the sum of integrals at the selected $\tau_{del}$. Increasing $\tau_{del}$ continuously by

$$\tau_{del}(t) = \frac{1}{\Delta f} t, \quad (6)$$

where $\Delta f = f_{pump} - f_{probe}$ is the frequency difference between pumping and probing signals, the recorded integrals at each point. Note that the sampling rate is completely independent from the pump frequency, thus the temporal resolution is limited by the minimum pulse width of the waveform-generator. We note that the pulsed probe signal is additionally amplitude modulated (AM) and the probe response is detected at the modulation frequency with a lock-in amplifier. Firstly, this is more sensitive (especially if a cantilever Eigenmode is chosen for the envelope frequency), secondly, it removes any spurious drift of the static cantilever bending. Another implementation of the pump-probe sampling can be realized by using pulse-width modulation (PWM) of the probing signal, where the duty cycle changes periodically with the modulation frequency:

$$\eta(t) = \eta_0 - \frac{1}{2} \eta_{depth}(1 + \cos \omega_{mod} t), \quad (7)$$

where $\eta_{depth}$ is the modulation depth. Here the time resolution is no longer limited by the pulse duty cycle ($\eta_0$) but rather the modulation depth ($\eta_{depth}$), which normally is set to be $\eta_{depth} < \eta_0$, and thus can result in superior temporal sensitivity and signal-to-noise ratio (SNR). In order to avoid the crosstalk in the topography channel, response time of the KPFM
feedback loop, and further complication of the KPFM setup reported by Murawski et al.\textsuperscript{25}, we implemented pump-probe KPFM in open-loop mode. Figure 1 of the main text represents the schematics of the employed setup with the electrical waveforms applied to the cantilever both for standard KPFM and pump-probe KPFM. For the latter one a PWM method was applied. The frequencies of the pulse trains were varied in order to record the appropriate time constants of the perovskite system. For single point measurements the probe was lifted at fixed distance above the sample, the mechanical tapping excitation and the z-piezo feedback was turned off and the modulated pulse signal was applied to the cantilever, resulting only in the electrostatic force acting upon the cantilever. Figure S4a shows a typical time trace of the first harmonic of the electrostatic force recorded in this way. In order to extract the time constants from the observed square-wave responses, the time traces were fitted with a Heaviside function with exponential growth and decay:

\[
f(x) = a_1 \frac{1}{1+E^{-2k_1(z-z_0)}} + a_2 \frac{1}{1+E^{-2k_2(z-z_0)}} - d. \quad (8)
\]

The reciprocal of the exponential factor multiplied by the repetition time and the frequency difference between the pulses gives the time constant on the correct timescale:

\[
\tau = \frac{1}{k} T_{rep} \Delta f, \quad (9)
\]

where \(T_{rep}\) is the repetition period and \(\Delta f\) is the frequency difference between pump and probe pulse. A repetition frequency of 50-150 kHz was selected for the pulses as it allows monitoring of microsecond timescale effects but can still be modulated by a sinusoidal waveform at the cantilever resonance frequency which improves sensitivity. The temporal resolution in a pump-probe configuration is defined by the duty cycle (pulse-width) of the probing signal. We note that although higher duty cycles (pulse-widths) lead to higher signal to noise ratios (SNR) (see Figure S4b inset), the overall temporal resolution of the measurement decreases as can be seen
in **Figure S4b**, where we show the measured and fitted time constants versus the probing pulse duty cycle in an amplitude modulated probe pulse measurement. The results show that the extracted time constant decreases with decreasing probe duty cycle. Once the pulse-width that matches or is lower than the time constant under investigation is reached a minimum appears and persists until the measured signal drops below the noise level. We note that at the 2 μs pulse-width the extracted response is still a convolution of the system response and the averaging effect of the probing pulse-width, leading to an error in the exponential fit. In contrast, the asymmetry seen in **Figure S4b** indicates that the slow relaxation is defined by the system response rather than by the applied pulse-width. In case of the map shown in **Figure 4.**, although, depending on the employed scanning speed the integration time changes for each pixel, as mapping was done at a constant phase-offset between the pulses, the contrast between pixels and the resulting maps is independent of the interplay of applied pulse and scanning frequencies. Optimum conditions for our measurements were reached at 1 μs pulse width.