Supplementary Information

Anomalously large interface charge in polarity-switchable perovskite photovoltaic devices: an indication of mobile ions in organic-inorganic halide perovskites

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1. The influence of the interface charge on band bending

In addition to the interpretation in the literatures¹, we propose another explanation of the influence of the interface charge on the band bending near the interface.



Figure S1. Schematic showing the change in band bending near the interface due to the interface charge. **a**, No change in band bending due to zero charge; **b**, Downward bending due to positive charges near the interface; **c**, Upward bending due to negative charges near the interface. Interface charge and screen charges are represented in red and black, respectively.

For convenience purposes, we assumed that the Fermi level of the perovskite is aligned with that of electrode. Without interface charge, no band bending occurs near the interface (Figure S1 **a**). If the positive charge with a density D=56 μ C/cm² appears near the interface (Figure S1 **b**), then a very high electric field E= D/ $\epsilon_0\epsilon_r$ =3.2×10⁹ V/m (if a dielectric ϵ_r =20 is assumed in the interface region) is formed between the interface charge in the perovskite and the screen charge on the electrode. The strong field sweeps out the holes toward the electrodes. Consequently, a large

amount of electrons accumulate in this region. Higher electron density means E_c is closer to E_F ; in other words, the band bends downward. The reduced barrier between E_c and E_F suggests the formation of Ohmic contact for electron injection. Similarly, if negative charge appears near the interface (Figure S1 c), then the band bends upward. The reduced barrier between E_v and E_F suggests the formation of Ohmic contact for hole injection.

2. Impedance spectroscopy measurement

A measurement of the dielectric-frequency characteristics (Figure S2) from impedance spectroscopy indicates that the relative dielectric constant continuously increases with decreasing frequency, from ~20 at 1 MHz to ~19,200 at 0.01 Hz. Very high value of > 10,000 was observed when the frequency was lower than 0.1 Hz. These values are in consistent with the large interface charge and the charge accumulation time of ~10 s.



Figure S2. Dielectric-frequency characteristics of the device ITO/PEDOT:PSS/MAPbI₃/MoO₃/AI.

3. Ferroelectric hysteresis measurement

The polarization-voltage hysteresis loops were measured at 300 K (Figure S3 **a**) and 77 K (Figure S3 **b**). The results show typical effect of leakage current. No ferroelectric hysteresis was observed even in liquid nitrogen temperature although the conducting current is two orders lower than at room temperature (Figure S3 **c**).



Figure S3. Ferroelectric hysteresis measurement. **a**, Polarization–voltage hysteresis loop measured at 300 K. **b**, Polarization–voltage hysteresis loop measured at 77 K. c, Change in the current density of the device under a constant bias of 1 V when the temperature is changed from 300 K to 77 K.

4. An estimation of the maximum polarization in MAPbl₃.

Suppose that ferroelectricity occurs in MAPbI₃, in order to estimate the maximum polarization, we assume the divalent Pb²⁺ ion shifts from the negative charge center (vertex) to the cubic center (Figure S4). The maximum dipole moment of a unit cell is $d_c = \sqrt{3}$ aq, and thus the maximum polarization of the material is $P_m = d_c/a^3 = \sqrt{3} q/a^2 = 71 \mu C/cm^2$, where q is the elementary charge and a=6.26 Å is the lattice constant².



Figure S4. Schematic showing the hypothesized shift of the Pb²⁺ ions in pseudo cubic MAPbI₃.

5. New polarity-switchable devices

We investigated two new devices, ITO/Cs₂CO₃/MAPbI₃/MoO₃/Al and ITO/PEDOT:PSS/MAPbI₃/Au. The preliminary results show considerable photovoltaic response from both devices (Figure S5).



Figure S5. J-V characteristics of two new polarity-switchable devices under one sun illumination. **a**, ITO/PEDOT:PSS/MAPbI3/Au. **b**, ITO/Cs₂CO₃/MAPbI₃/MoO₃/AI.

6. J–V characteristics under dark condition



Figure S6. Current–voltage characteristics of the device ITO/PEDOT:PSS/MAPbI₃/MoO₃/AI in forward and backward scans under dark conditions. The inset is the semilog plot of the J–V curves.

Under dark conditions, the J–V curve shows symmetrical feature at positive and negative biases, which violate the asymmetric conductance of a conventional diode (Figure S6). Significant current conduction occurs at positive bias over 1.0 V and at negative bias below -1.0 V. The dark J–V curves also show hysteresis. The semilog plot of the J–V curves is shown in Figure S6 inset. An important and unusual phenomenon is the non-zero Vocs of the dark J–V curves, suggesting that the device undergoes a thermal nonequilibrium process at zero bias. This nonequilibrium process is the relaxation process of the interface charge.

7. The influence of the preset voltage



Figure S7. The influence of the preset voltage on the performance of the devices. **a**, J-V characteristics of the photovoltaic device under one Sun illumination with/without the preset voltage. **b**, J-V characteristics of the photovoltaic device under dark with/without the preset voltage.

The applied preset voltage accumulates more interface charge before the scan, and thus enhances the measured parameters (Isc, Voc and FF) of the photovoltaic response as indicated in Figure S7 a. This is in consistence with the dark J-V characteristics (Figure S7 b), which shows higher Voc value with the preset voltage than without it.

8. The correlation between the dynamic change of the interface charge and the photocurrent.



Figure S8. The correlation between the dynamic change of the interface charge and the photocurrent. **a**, The relaxation current of the interface charge under dark condition. **b**, The dynamic change of Isc under one Sun illumination after removal of the pre-applied voltage.

Under dark condition, a bias of 2.0 (-2.0) V was applied on the device for 12 s to accumulate the interface charge. The device was then kept at a short circuit condition to observe the non-zero current, which indicate the relaxation of the interface charge (Figure S8a is the same as Figure 2 inset). Similarly, under one Sun illumination, a bias of 2.0 (-2.0) V was applied on the device for 12 s to accumulate the interface charge. The device was then kept at a short circuit condition to observe the dynamic change of the photocurrent (Figure S8 b). The interface charge relaxes in a time scale of ~20 s. The photocurrent decreases and stabilized in the same time scale. The apparent correlation suggests that the vanishing interface charge leads to the decrease of photocurrent, indicating that the dynamics of the interface charge determines the photovoltaic performance of the device.

9. Multiple J-V scans with different scan range



Figure S9. Multiple J-V scans of the device ITO/PEDOT:PSS/MAPbI₃/MoO₃/AI with different scan range under one sun illumination.

Figure S9 shows the J-V characteristics of the device with loop scans, for example, from 1.0 V to -1.0 V and immediately from -1.0 V to 1.0 V. The shape of the J–V curves shows apparent hysteresis loop. The loop with a small scan range (e.g., -0.1 V to 0.1 V) sits in the inner circle of the loops and expands with a wide scan range. When the scan range is -1.0 V to 1.0 V, both the forward and reverse scans pass through the fourth quadrant (we define ITO/PEDOT:PSS as ground, the scan from positive to negative as forward scan, and that from negative to positive as backward scan). No loop lines cross the second quadrant, indicating that the polarity of the device is not changed during the scan, which is similar to most reported hysteresis. However, the reverse scan unexpectedly passes through the second quadrant when the voltage range surpasses -1.0 to 1.0 V, indicating that the polarity of the device is changed during the scan.

10. The photocurrent response under constant bias



Figure S10. Photocurrent response the device as a function of time under constant bias with one sun illumination.

Under constant bias, the accumulation of the interface charge significantly influence the function of the device and thus leads to the variation of the photocurrent (Figure S10). For example, under 0.6 V bias, at the beginning stage the device is not a functional photovoltaic device (the current is positive), and after ~10 s, it becomes a diode and begins to show photovoltaic effect (the current becomes negative). However the steady photocurrent is much lower than that predicted by the J-V characteristics with preset voltage (Figure 2 in the main text), indicating the device is not an efficient solar cell. This switchable photovoltaic device may have other potential application.

It seems that this result contradicts Figure 3, because Figure 3 suggests that higher constant bias stabilize the charge more rapidly and provide better PV performance. However the different PV performances should be represented by a series of J-V curves instead of single point. Better performance should have higher Voc and Jsc value as sketched in Figure S11. The measured photocurrent at 0.2 V, 0.4 V, 0.6 V and 0.8 V in Figure S10 are only single point (named a, b, c and d, respectively) on the different J-V curves. Therefore the results in Figure S10 do not contradict the conclusion from Figure 3. We note that in Figure S11 the J-V curves are not totally imagined, they are sketched with a reference to the curves in the 4th quadrant of Figure S9.



Figure S11. Schematics showing the results of Figure S10 are scatters on a series of different J-V curves.

11. The evolution of the band-diagrams

Figure S12 shows the evolution of the band-diagrams due to the accumulation of the interface charge under forward and backward (preset) bias. After the accumulation of the interface charge and changing the bias to zero, the band-diagrams will be like the ones in Figure 1e and 1f.



Figure S12. The evolution of the band-diagrams due to the accumulation of the interface charge under forward and backward bias. **a**, Zero bias, no interface charge in the virgin state. **b** (e),

Forward bias (Backward bias), at the beginning there is no interface charge. **c (f)**, Forward bias (Backward bias), after several seconds the interface charge is formed. The band bends downward (upward) at the interfaces with positive (negative) interface charge. **d (g)**, quickly change the bias to zero, the band-diagram is the same as Figure 1e (f).

12. A brief introduction of the measuring process.

In our measurement, the duration between the voltage pre-biasing and the PV measurement is zero, because the Source-Measure Unit (Agilent B2902A) that we used is a programmable power supply and we can put the voltage pre-biasing and the I-V scan into one process. The measuring process is illustrated in Figure S13.



Figure S13. Illustration of the measuring process with the programmable power supply. **a**, After the pre-biasing, the device is kept at zero bias to measure the short-circuit current (Isc). **b**, The I-V scan is right after the pre-biasing.

13. The non-exponential decay of the relaxation current.

Figure S8 b indicates that the lsc under illumination with 2.0 V preset bias would finally stabilize at certain non-zero value, while the lsc will become almost zero with -2.0 V bias. These two lsc do not meet each other in the figure. In order to understand this phenomenon we reexamined the dynamics of the relaxation current in Figure S8 a. Figure S14 shows the semilog plot of the relaxation current. It shows non-exponential decay. The current decays very fast at the beginning, but it decays more and more slowly over time. This means that the interface charge decreases very fast at the beginning, but it declines more and more slowly over time. It also means that it will take a very long time for the interface charge to completely vanish. This is the reason for the observed result (in Figure S8 b) that the lsc under illumination with 2.0 V preset bias does not meet the lsc with -2.0 V bias in the relatively short period of time. The asymmetrical lsc from 2.0 V and -2.0 V preset bias is due to the slightly asymmetrical property of the electrodes (the work function of MoO₃/Al is slightly higher than that of PEDOT:PSS/ITO).



Figure S14. Semilog plot of the relaxation current of the interface charge.

14. An estimation of the capacitive effects in the J–V measurement

There is strong capacitive behavior in the device due to the existence of mobile ions in the perovskite layer. The capacitance can be estimated from the measured interface charge density under certain bias. For example, the interface charge density can reach D=56 μ C/cm² under V=2.0 V bias (Figure 4a), thus the capacitance (per unit area) reaches C = D/V=28 μ F/cm². This large capacitance is consistent with the measured very large relative dielectric constant (ϵ_r >10000) in

Figure S2 if we consider the relation C = $\varepsilon_0 \varepsilon_r/L$, where L = 480 nm is the thickness of the perovskite layer.

Figure S9 shows the J–V scans of the device with different scan range under illumination. Figure S15 shows the J–V curves with different scan rates. The shape of the J–V curves shows apparent hysteresis. Our results suggest that the dynamic change of the interface charge leads to the functional change of the device and thus cause the J–V hysteresis. The large capacitance of the device should also contribute to the hysteresis because of charge and discharge processes in the loop scans. However, this capacitive contribution is not significant due to the following reasons. Firstly, the capacitive behavior should also present in the dark J–V curves. But the dark current under forward scan and backward scan (Figure S6) in the range of -1 V to +1 V are all very small and do not show significant difference. Secondly, the difference of current between forward scan

and backward scan due to capacitor charge and discharge is $\Delta J = 2J_c = 2\frac{dq}{dt} = 2C\frac{dV}{dt} = 2CR$,

where J_c is the charging current, C is the capacitance, R is the scan rate. If C = 28 μ F/cm², R = 1 V/s, the resulting current difference is $\Delta J = 0.056 \text{ mA/cm}^2$, which is two orders of magnitude lower than the measured difference of photocurrent (4 – 30 mA/cm² at 0 V) between forward and backward scan in Figure S9 and S15. Thirdly, the capacitance-related current difference ΔJ should be proportional to the scan rate R, but the hysteresis in Figure S15 is not proportional to R. Finally, if the scan rate R is higher than 20 V/s, ΔJ could reach 1 mA/cm², indicating that at the high scan rate the capacitive effect cannot be ignored anymore. This analysis is consistent with the view of Snaith et al.,³ which expresses that below the scan rate of 15 V/s errors from capacitive effects are minimized.



Figure S15. J–V curves with different scan rates under one Sun illumination.

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