Unravelling the Factors Influencing Halide Perovskite Based Switchable Photovoltaics

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Lead halide perovskites have revolutionized the field of optoelectronics (such as photovoltaics and light emitting diodes) demonstrating extraordinary material properties despite being formed at low temperatures. However, ion migration in the bulk or at the interfaces results in stability issues especially in devices where metal electrodes directly interface with the perovskite film. Utilizing the switchable photovoltaic phenomenon (SPV) in halide perovskites as a measure of ion migration and electrochemical reactions within them, Cs_{0.05}MA_{0.15}FA_{0.70}PbI_{2.5}Br_{0.5} triple cation perovskite, widely used in photovoltaics is evaluated. The various factors determining the SPV, including electric field magnitudes, type of metal contacts, Illumination conditions, and temperature is systematically measured. This study reveals the roles of electrode work functions and reactivities on ion migration and local electronic structure modulation. ITO electrodes demonstrated the highest open-circuit voltage (V_{oc}) about 0.85 V while Ag electrodes developed conductive filaments. However, the V_{oc} distribution for Ti and Cr electrodes shows a more pronounced linear correlation with the poling electric field strength. Insights from this lateral design are directly relevant to transistor and memristor architectures and offer inputs into the design of perovskite-based photovoltaic/optoelectronic devices.

1. Introduction

In recent years, lead halide perovskites (LHPs) have gained substantial attention owing to their exceptional characteristics, including a high optical absorption coefficient,^[1] low trap density,^[2] bipolar transport properties,^[3] and tunable bandgap.^[4,5] These

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properties have led to rapid advancements in perovskite solar cells,^[6–9] perovskite light-emitting diodes,^[10,11] perovskite photodetectors,^[12] etc. In addition, advancements have also been made on perovskite-based optoelectronic devices that feature conducting electrode/perovskite interfaces, such as SPV,^[13,14] artificial synapses,^[15,16] field-effect transistors,^[17–19] and resistive switching devices.^[20–22]

Complex physical, chemical, electronic, and optoelectronic interactions exist at the LHP/electrode interface. Current research on LHP/metal contacts have focused on band bending,^[4,23,24] charge transfer,^[25,26] carrier recombination,^[27] LHP degradation,^[20] various electrode modifications,^[28] and their utility in electronic devices. In addition to typical considerations of semiconductor/ electrode interfaces, halide perovskite-based interfaces need to consider intrinsic and extrinsic ionic activities of the LHP as well as the possibility of its reaction with the electrode. It may involve diverse reaction mechanisms, which is crucial

for understanding its electrochemical properties and performance. In terms of reactivity, LHP/Ag interfaces have been reported to react and generate various products, such as metallic Pb⁰, mobile Ag⁺ ions, and gaseous I₂.^[29,30] Similar reactions and diffusion of "inert" Au into perovskite have also been reported.^[31]

The switchable photovoltaic effects in lateral structures could be a powerful tool to examine such ionic migration efforts as well as reactivity considerations. In addition, due to the similarity of SPV device structure to transistors and lateral memristors, these insights can be applied to the different device classes. The SPV phenomenon is purported to arise from the rearrangements of ions in perovskite film induced by an electric field.^[13,32] The poling current reflects the dynamic process of ion migration or chemical reactions, while the V_{oc} and short circuit current (I_{sc}) provide insights into the state of the system after poling. In previous studies, Xiao et al explored the effects of electric fields and light modulation on the V_{oc} of lateral SPV device ^[32] while our previous work demonstrated SPV effects in lead-free perovskites.^[33,34] Nonetheless, there has been no investigation thus far into the effect of metal contact on V_{oc} as well as the dynamics of the process through which the $V_{\mbox{\scriptsize oc}}$ arises. Thus, it is essential to thoroughly investigate the physical and chemical

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Figure 1. Device structure to study the switchable photovoltaic phenomenon. a) Schematic of the lateral structure devices. Both bias and illumination can be applied directly on the perovskite film. b) The optical image of the electrode (upon-left) and devices, electrode gap: 20 μ m, electrode length: 100 μ m. c) SEM image of perovskite film, inset is statistical information of grain size. The average size of grains is 226 nm. d) *I–V* curve of the device before and after negative and positive poling (±1.5 V μ m⁻¹ for 20 s), light intensity is 10 mW cm⁻², light wavelength is 623 nm, sweeping rate is 0.05 V step⁻¹; the arrows in the figure indicate the scanning direction. e) Schematics of ion state in perovskite film during positive poling, respectively, showing that accumulated ions in the perovskite near the electrodes induced p- and n-doping. The corresponding energy diagrams are below.

properties of the LHP/metal interface, interface electronic structure, and charge carrier behavior to comprehend the mechanism and achieve better control of these devices.

In this study, we examined the impact of electric field conditions and various electrodes on SPV. These metals directly interface with the triple-cation perovskite (Cs_{0.05}MA_{0.15}FA_{0.70}PbI_{2.5}Br_{0.5}, CsMAFA) layer with differences in energy levels and chemical reactivity, and therefore form interfaces with varying charge injection energy barriers and recombination dynamics. We systematically investigate band engineering, electrode corrosion, and electrochemical reactions at the interfaces, employing metals with varying work functions and reactivity, including Au, Ag, ITO, Pt, Cr, and Ti. The results demonstrated that the selection of the metal electrode has a substantial impact on both the values and distributions of $V_{\rm oc}$, which is explained by an energy band model and chemical reaction model that we propose. Furthermore, we explore the effects of illumination and temperature on SPV performance to further elucidate the effect of ionic migration on the SPV mechanism. Finally, we attempt to directly examine the self p- and n-doping effect in perovskite film through Kelvin probe force microscopy (KPFM) characterization, a technique capable of mapping the surface potential of the perovskite film after the poling process.

2. Results and Discussion

2.1. Device Structure and Switchable Photovoltaic Phenomenon

Although halide perovskites of various compositions have been studied, we have chosen a composition that has been widely reported to be more thermally stable, phase-pure and less prone to degradation by a wide variety of research groups -CsMAFA, where FA and MA represent formamidinium and methylammonium.^[35,36] A symmetrical lateral structure of electrode/CsMAFA/electrode is adopted, which bears close functional resemblance to lateral memristors and bottom-gate transistors^[37] as shown in **Figure 1**a. The patterned metal electrodes are fabricated via a lift-off process through thermal evaporation on a silicon oxide (SiO₂) substrate. The CsMAFA perovskite film is subsequently formed via antisolvent assisted spin-coating process (See method section and Figure S1, Supporting Information). Figure 1b shows the optical image of device structure, indicating that the perovskite is uniformly coated on the substrate. The lateral gold electrodes have a spacing of 20 µm and width of 100 µm. The absence of any discernible color variation between the channel and electrode suggests the uniform distribution of perovskite on the substrate. Previous studies have highlighted the significant impact of grain size on ion migration within perovskite films.^[38] Therefore, it is imperative to conduct a statistical analysis of the CsMAFA grain size and maintain this variable constant throughout all experiments. Figure 1c displays a scanning electron microscope (SEM) image of CsMAFA along with statistical data regarding the grain size. The image reveals uniformly arranged grains with an average size of 226 nm. Ion migration occurs within the material during electric poling, contributing to current hysteresis and various other distinctive properties of perovskite electronics. As an example, when the device is measured by a sweeping voltage, it displays a significant hysteresis with different sweeping speeds (Figure S2a, Supporting Information). This illustrates field-induced ion migration, akin

to a memristive effect and produces a current output (Figure S2b, Supporting Information) correlated with the scanning history when biased with a 0.05 V step⁻¹ sweeping voltage. Consequently, it is understandable that electric fields of varying orientations can control the migration of ions and the direction, leading to the accumulation/depletion of ions and the formation of locally doped regions at the LHP/metal interfaces.^[39] Figure 1d and Figure S3 (Supporting Information) shows the dark current and photocurrents measured before and after the poling of the device with a 20 µm electrode spacing. First, the device shows very little current under dark conditions, comparable to the limit of the measuring equipment. As anticipated, the lateral device does not manifest any photovoltaic behavior ($J_{sc} = 0$, $V_{oc} = 0$) before electrical poling. While photogeneration occurs in the perovskite absorber layer and leads to an increase in photoconductivity in the film, charge separation is not possible without an externally applied voltage. This is due to the symmetrical electrode architecture without any built-in field to facilitate charge separation and collection. However, after applying a constant bias voltage of 10 V (equivalent to an electric field of 0.5 V μ m⁻¹) to the device for \approx 20 s at RT, followed by *I*–*V* sweeping measurement with illumination intensity is 10 mW cm⁻² (wavelength: 623 nm), a distinct V_{oc} of 0.35 V and a I_{sc} of \approx 5 nA were measured. Under reversed poling conditions, the device demonstrated reversed behavior in $I_{\mbox{\tiny sc}}$ and $V_{\mbox{\tiny oc}}$, a phenomenon referred to as the SPV effect. The observed SPV phenomenon might arise from the reversible formation of distinct self p-doped and n-doped regions within a single perovskite bulk layer. Figure 1e depicts the electric field poling process on the perovskite film, accompanied by energy diagrams at each stage. Initially, prior to the application of an external electric field (e-field) for poling, the device remains in an equilibrium state (i) with a flatband condition because of the symmetry of the electrode work function under both dark and illuminated conditions. Upon the application of an external bias to the device, ions/vacancies within the perovskite layer migrate in response to the applied electric field. Accumulated positive ions/vacancies on one side of the perovskite layer function as space charges, inducing n-type doping in localized regions. In a later section, the charge potential distribution of the electrically poled surface can be further observed with Kelvin-probe force microscopy measurements. Meanwhile, the remaining negative space charges induce p-type doping on the opposing side, forming a p-i-n or n-i-p homojunction, leading to band bending (ii). However, the localized doping induced by ion migration is insufficient to enable the film to generate voltage under dark conditions. As shown in Figure S3 (Supporting Information), the dark current exhibited negligible differences after both positive and negative poling, with no generation of V_{oc}. Only when the device is exposed to light, photogenerated electron-hole pairs are generated and separated, moving toward opposite ends of the energy band, resulting in the generation of V_{oc} and I_{sc} .

2.2. Electric Field Effect on SPV

Generally, a higher electric field could be expected to induce more ions to drift and therefore result in a higher accumulation/depletion of ions at the interface. Exploring the connection between electric field strength and V_{oc} is of significant interest as we study the drift, accumulation, and doping dynamics of the perovskite film during the poling process. Figure 2a illustrates the correlation between the poling current and the electric field strength of the device (poling time = 16 s). When the electric field increases beyond 1 V μ m⁻¹, the current is relatively low at the outset of the poling process, with increasing poling time, the current rises and eventually reaches a near-saturated state. In this process, the initial current results from a combination of charge transport and ion migration. The saturated state can be understood as the physical limit of ionic accumulation/depletion at the interface and the complete stoppage of ionic currents. A higher electric field leads to a faster increase in poling current and a correspondingly larger saturation value. However, when the device was subjected to a larger bias, the current might display a trend of initial increase followed by a decline (Figure S4, Supporting Information), attributable to possible charge transfer processes of Faradaic nature at the interface which could be undesirable in our study. Figure 2b displays V_{oc} and I_{sc} measurements taken immediately after each poling cycle (illumination intensity: 10 mW cm⁻², light wavelength: 623 nm), both exhibits an upward trend with increasing electric field strength. Moreover, even at a small electric field of $0.2 \text{ V} \mu \text{m}^{-1}$, a V_{oc} close to 0.2 V is generated, suggesting that even a very small electric field can induce ion migration. It is important to note based on Figure 2c, that V_{oc} and I_{sc} do not exhibit a clear linear relationship with the electric field. Furthermore, as the device is subjected to higher electric fields, increment of I_{sc} (ΔI_{sc}) exhibits a progressively greater increase, while the increment in V_{oc} (ΔV_{oc}) diminishes (Figure S5, Supporting Information). This phenomenon can be attributed to autonomous ion diffusion following the cessation of the poling bias. As previously mentioned, V_{oc} arises from the p- and n-doping formed through ion migration under the influence of electric field; hence, a larger electric field results in a more pronounced ion migration, leading to a higher V_{oc}. Simultaneously, after the removal of the electric field, ions begin to diffuse back, causing the ΔV_{oc} to diminish. Figure 2d,e depict the poling current and photovoltaic parameters (V $_{\rm oc}$, and I $_{\rm sc}$) under negative poling conditions, respectively. These results closely mirror the findings under positive poling conditions, suggesting that after poling in different directions, the distribution of ions has a symmetrical composition and morphology in the horizontal plane. Besides electric field strength, the duration of poling may also influence ion migration within the material, consequently impacting the SPV performance. Table S1 (Supporting Information) compared the reported SPV effect. Among them, this device shows higher short-circuit current density compared with other lateral devices. Figure 2f illustrates the association between V_{oc} value and poling time at various electric fields (Figure S6 shows the I-V sweeping curve, Supporting Information). At electric field strength of 0.2 V μ m⁻¹, V_{oc} reaches 0.25 V after 50 s of poling, while at 2.0 V μ m⁻¹, V_{oc} reaches \approx 0.45 V after 50 s then reaches 0.52 V after 80 s of poling, with minimal further increase for longer poling durations. This phenomenon occurs due to ion migration reaching saturation after a period under a constant electric field. For instance, at an electric field strength of 0.5 V $\mu m^{-1},$ V_{oc} exhibits minimal further increase after 60 s, suggesting little distinction in ion migration between 60 s and durations exceeding 60 s. The findings also indicate that at higher electric field strengths, ion migration may require a more extended period to reach

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Figure 2. Electric field strength dependence on the magnitude of SPV. a) Positive poling current of the Ti/CsMAFA /Ti lateral structure (electrode gap is 20 μ m) device, electric field are ranging from 0.2 V μ m⁻¹ to 5.0 V μ m⁻¹, poling time:16 s. b) Photocurrents of the device after each positive poling, sweeping rate of 0.05 V step⁻¹, illumination intensity :10 mw cm⁻², light wavelength: 623 nm. c) Summarized V_{oc} and I_{sc} of lateral devices with different poling electric fields. d) Negative poling current of the Ti/CsMAFA /Ti lateral structure (20 μ m) device. e) Photocurrents of the device after each negative poling f) Summarized V_{oc} of lateral devices with different poling time and electric fields.

saturation. Alternatively, it is plausible that this could result from higher electric field driving more ions to migrate. In summary, the migration of ions is influenced by the combined impact of the electric field and the duration of poling, carrying significant implications for the operation of devices based on LHP.

2.3. Effect of Metal/Perovskite Contact on SPV

The understanding of the influence of metal contact on the stability and performance of photovoltaic and other optoelectronic devices is still evolving. With the absence of built in electric field, symmetrical perovskite devices offer a platform that is convenient to observe electrochemical occur reactions at the interface under electrical bias. In this work, we fabricate devices with different electrode metals (Cr, Ti, Ag, Au, ITO, Pt) to investigate the impact of varying work functions and chemical reactivity on SPV. **Figure 3a** and Figure S7 (Supporting Information) illustrates the work functions of these electrodes, measured using ultraviolet photoelectron spectroscopy (UPS), with horizontal lines representing reported values and circles indicating measured values in this work, along with error analysis from three different regions of each electrode. Figure 3b schematically shows the relative positions of the metal work functions and bandgaps of n-type perovskite semiconductors. Our results show that the deposited triple cation perovskite (CsMAFA) behaves like a weakly doped n-type semiconductor with low Fermi level (4.15 eV) and Valence band maximum (1.73 eV) positions. High work function materials exhibit a substantial energy difference between the electrode work function and the perovskite Fermi level (E_{r}) , leading to band bending in the conduction band and the formation of a high Schottky barrier for electron injection, requiring thermal activation (thermal ion emission) to overcome this barrier (Figure S8a, Supporting Information). Conversely, low work function metals, with their lower Schottky barrier heights, have a higher electron injection into the semiconductor material (Figure S8b, Supporting Information). However, low work function metals such as Al typically exhibit lower electrochemical reduction potential (higher tendency to be oxidized) and shown to have higher chemical reactivity, potentially reacting with perovskite.^[40,41] Figure 3c schematically illustrates two potential reactions: oxidation reactions occurring at the anode and reduction reactions at the cathode. In Figure 3c(i), reactive metals undergo oxidation and migrate into the perovskite material as M⁺ ions. Some M⁺ may be reduced back to M⁰ metallic particles due to the injection of electrons from the cathode, while others may undergo a two-step reaction pathway with halide anions (I⁻, Br⁻) near the anode, generating halides. Figure 3c(ii) presents an alternative scenario

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Figure 3. Effect of metal/perovskite contact on SPV. a) Work function of different electrodes and perovskite (PVK). b) Schematics of the relative energy positions between perovskite bandgap and metal work function (Φ). c) Schematics of reaction between electrode and perovskite. i. The metal is oxidized and subsequently reacts or reduced during migration. ii. Lead ions (Pb⁺) are reduced at the cathode and iodide ions (I⁻) are oxidized at the anode. d–f) Summarized V_{oc} of ITO, Ti, Pt electrode devices with different poling electric fields and electrode spacings. g,h) Summarized saturated V_{oc} of ITO, Ti, Pt electrode devices mutated electrode spacings. Error bar is based on five devices. i) Summarized saturated V_{oc} of lateral devices (20 µm) with different electrode. j) Switching behavior of lateral Ag electrode devices.

where low work function metals with work functions close to the conduction band minimum (CBM) of CsMAFA promote efficient electron injection. However, due to the higher electronegativity of Pb compared to these metals, Pb^{2+} ions are more readily reduced than the electrode metal ions themselves, forming Pb^0 at the negative-biased electrode. Another possible chemical reaction is that iodide ions (I⁻) in the perovskite layer migrate from the perovskite layer to the anode, where they participate in an electrochemical reaction and are oxidized to a gaseous I_2 product.

Figures 3d–f and Figures S9–S11 (Supporting Information) show the trends in $V_{\rm oc}$ for different metals with varying electric

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fields and electrode spacings, all with a poling time of 15 s. First, ITO exhibits work functions close to the perovskite Fermi level, indicating that electrons can efficiently transport without overcoming significant barriers. Additionally, ITO does not seem to react chemically with perovskite, causing any interfacial doping or formation of insulating interface barrier. Therefore, upon poling, the V_{oc} rapidly increases with applied electric field, approaching ≈ 0.7 V under 2 V μm^{-1} poling electric field, before slowly approaching the saturation value (0.85 V). The ITO electrode device demonstrated the largest V_{oc} compared to other electrodes. Poling effects in both positive and negative biases exhibit symmetrical characteristics. Notably, except for the 50 µm device, the maximum applied electric field is $4 \text{ V} \mu \text{m}^{-1}$ for all devices, as the maximum applied bias by the semiconductor analyzer is ≈ 210 V. Devices with Ti electrodes show a different trend, with V_{oc} reaching only ≈ 0.4 V within the electric field range of 0.2 to 5 V μ m⁻¹. This could be due to the formation of a thin film of metal oxide (TiO_x) widely used as a transport layer selective to electrons in solar cells at the anodic Ti surface, weakening the homojunction formation in the perovskite film. We performed X-ray photoelectron spectroscopy (XPS) analysis of the Ti electrode surface (Figure S12, Supporting Information) and found signatures of the oxidation state in the Ti electrode. Sub-stoichiometric TiO, could also contain high levels of deep defect states which could accelerate recombination and therefore weaken the resultant photovoltage generation. Similarly, the Cr sample, which also has a low work function, exhibits an initial increase in poling current but is subsequently followed by a decrease (Figures S13 and S14, Supporting Information). This may be attributed to the reduction of Pb^{2+} ions at the cathode, deteriorating cathode electron injection. However, the broader distribution of V_{oc} (0.4–0.7 V) suggests that other electrochemical processes at the anode may also contribute to this effect. Furthermore, devices with Ti electrodes exhibit a more linear distribution of V_{oc} with increasing electric poling. This is due to the smaller barrier difference at the Ti (TiO_v)/perovskite interface and the collective influence of the presence of TiO_x. In addition, the value of V_{oc} tends to increase with larger electrode spacings, but the slope of the linear fit becomes smaller. This suggests that if the electric field intensity during poling continues to increase or poling time is extended, V_{oc} will no longer depend on electrode spacing. As shown in Figure 3g and Figure S15 (Supporting Information), performing multiple cycles of poling with a larger electric field of 10 V μm^{-1} on devices (Figure S16, Supporting Information), until V_{oc} no longer significantly increases, yielded saturated V_{oc} values. As expected, the saturated V_{oc} remains relatively consistent across different electrode spacings in the same electrode configuration. However, variations in V_{oc} are more pronounced when comparing different electrode materials, which means saturated V_{oc} depends on the electrode material but independent of electrode spacing. Au and platinum (Pt) are two commonly used noble metals in the configuration of solar cells. They are preferred due to their relatively high inertness to perovskite materials. Figure S17 (Supporting Information) illustrates a comparison of their poling currents with the same electrode spacing and poling conditions. Notably, Pt exhibits a lower poling current compared to Au. This disparity is attributed to Pt having a higher work function than Au. Consequently, when electrons enter the Pt electrode, they encounter a higher energy barrier, making electrons more difficult to flow from the metal to the perovskite, resulting in low current. When the poling bias is fixed at 16 s, although the V_{oc} of Pt electrodes shows a certain linearity with the poling electric field, as depicted in Figure 3f. The high energy barrier also results in a significant voltage drop at the LHP/metal interfaces, leading to a less effective electric field and ionic drift current across the perovskite bulk layer. As a result, an overall reduction in V_{oc} is measured. Figure 3h presents the statistical distribution of V_{oc} for Pt electrode devices after multiple poling cycles. Compared to other metals, Pt demonstrates a decreasing trend in saturated V_{oc} with increasing electrode spacing. This result validates the significant voltage drop due to the Schottky barrier height induced by high work function metals when biased. This observation underscores the crucial role of electrode work functions and the energy levels at the perovskite band in determining V_{oc} . Following positive poling, the distribution of V_{oc} is relatively narrow. However, after negative poling, $V_{\rm oc}$ exhibits a wide range across the five devices, ranging from 0.22 to 0.74 V. This variation may be attributed to the influence of poling sequences amplifying the effects of high-energy barriers. Typically, the device undergoes positive poling, followed by data collection, and then switches to negative poling for subsequent data gathering. During the measurement process, the positive poling has induced the formation of localized doping regions and the redistribution of charges within the perovskite layer. These induced alterations have the potential to influence the subsequent negative poling process, thereby contributing to a wider distribution range of V_{oc} values.

Figure 3i illustrates the relationship between saturated V_{oc} and work function for devices with an electrode spacing of 20 µm. In devices where no obvious chemical reactions occur at the electrodes, V_{oc} decreases with an increase in electrode work function. However, in devices where obvious chemical reactions occurs, the distribution of V_{oc} is not as extensive as expected, except for silver (Ag). This is because silver, being a highly reactive metal, undergoes severe chemical reactions with the perovskite material. Regardless of whether it is during the poling process (dark current) or under illumination conditions, a current consistently reaches the compliance value, as demonstrated in channels as small as 50 µm (as shown in Figure 3; Figure S18, Supporting Information). Figure 3j demonstrates the threshold switching behavior observed during the SPV testing process. In contrast to the typical current levels of 10^{-9} or 10^{-8} A, the current hits the compliance current limit (10^{-7} A) and subsequently returns to a high-resistance state as the scanning voltage decreases. This behavior is quite common in Agbased memristors, indicating the formation of a complete conductive filament (CF) path, we record a CF image under the optical microscope as shown in Figure S19a (Supporting Information). Furthermore, Ag can even spontaneously react with the perovskite film without the application of an external bias. Figure S19b-d (Supporting Information) illustrates the appearance of Ag electrode devices after two days of fabrication. It is evident that a black reaction product has formed at positions where the electrode surface overlaps with the perovskite. This reaction even occurs in devices that have not been biased, further confirming that the performance of Ag electrode devices is no longer suitable considered as a control group for discussion.



In addition to the work function and chemical stability of electrodes, conductivity may also influence the SPV phenomenon. Hence, we evaluated the resistance using I-V testing and the four-probe method respectively, which is to avoid errors caused by single method testing. As shown in Figure S20 and Table S2 (Supporting Information), the resistances of different metals show large differences, yet remains lower than the resistance of the perovskite used in this study, which exceeds 10⁹ ohms, (extracted from Figure S3, Supporting Information). Consequently, electrode resistance does not significantly influence the current flow within the device. Furthermore, the resistance values of different electrodes, in ascending order, are as follows: Ag < Au < Pt < ITO < Cr < Ti. This sequence does not show a direct correlation with the distribution of V_{oc} values mentioned earlier. Notably, during the poling process, Pt electrodes display the lowest poling current, which also deviates from the order of conductivity. Hence, the conductivity of electrodes is not a predominant factor influencing the SPV performance. The performance of V_{oc} and I_{sc} is more determined by the energy barrier and chemical reaction of the electrode/perovskite interface.

2.4. Light and Temperature Effect on SPV

Deng et al. reported the phenomenon of light-induced self-poling in perovskite materials. However, the phenomenon was observed in systems that employ asymmetric electrodes with an intrinsic built-in electric field, that might have facilitated the migration of ions in the perovskite. Therefore, it is essential to investigate whether illumination contributes additionally to photovoltaic parameters (V_{oc}/I_{sc}) in symmetric electrode devices.^[42] Figure 4a illustrates the photoconductivity read at 0.1 V of Ti/CsMAFA/Ti devices to red (632 nm), green (525 nm), and blue (445 nm) light before poling, showing a sensitive photocurrent response. It is noteworthy that the device exhibits a stronger photocurrent response when exposed to longer-wavelength light. This is because in lateral configuration, the active device resides close to the substrate. As the absorption coefficient of the perovskite is higher for light with a shorter wavelength, light with a shorter wavelength would be absorbed before reaching the active device area. On the other hand, longer wavelength light can be transmitted through the thickness of the film and be absorbed close to the active device region near the substrate and the electrodes. A good linear relationship is observed in the photocurrent (measured at 0.1 V) for all RGB (red, green, blue) stimuli as the light power increases from 10 to 100 mW cm⁻². To investigate whether light exposure induces effects similar to an externally applied electric field, the device was subjected to higher-intensity illumination (100 mW cm⁻²) instead of electric poling. As shown in Figure 4b, with pre-illumination durations ranging from 0 to 30 minutes, there was only a slight variation in photocurrent (within acceptable measurement error), and no obvious V_{oc} was generated. This suggests that even under strong and prolonged illumination, light cannot induce apparent ion migration in symmetric electrode systems without a built-in voltage (preset V_{bi}). During the V_{oc} testing process, illumination is typically initiated immediately after poling, with the illumination duration matching the voltage sweep time, whose duration (1 s) is insufficient to influence the ion migration state. Taking red-colored (623 nm) light as

an example, the device underwent multiple cycles of poling with a 1 V μm^{-1} electric field (electrode spacing = 20 μm) until V_{oc} reached a saturation value. Then, V_{oc} and I_{sc} were measured under different light conditions, with additional poling performed between changes in light intensity. The results are presented in Figure 4d (623 nm), 4e, and Figure S21 (Supporting Information), indicating that varying light wavelength and intensity primarily affect photocurrent (I_{sc}) while the measured V_{oc} is relatively constant. Statistical information in Figure 4c demonstrates a positive correlation between I_{sc} and electric field strength as well as light intensity, with I_{sc} influenced by both factors.

Due to the sensitivity of ion migration processes to temperature conditions, we conducted a study on the SPV effect over a wide temperature range (123 to 348 K). Lateral CsMAFA devices were placed at different temperatures, and the current values under a 0.3 V μ m⁻¹ electric field are shown in Figure 4f. It is observed that the dark current increases with rising temperature. However, at high temperatures, the dark current results from both ion and charge movement, whereas at sufficiently low temperatures, the dark current may be primarily contributed by electrons and holes. We established the relationship between device conductivity and temperature and determined the activation energy (E₂) for ion migration using the Arrhenius equation. As illustrated in Figure 4g, the red curve represents conductivity under dark conditions and exhibits two distinct linear regions. The activation energy in the high-temperature region is 0.46 eV, while in the low-temperature region, it is only 0.048 eV, a value closely matching that of the blue curve. The blue curve reflects the relationship between conductivity and temperature under illuminated conditions, which is primarily influenced by photo-generated electrons and holes. Thus, it closely resembles the activation energy at low temperatures. Due to the higher activation energy of electric field induced ion migration, it dominates mainly at relatively high temperatures (310-350 K).[13,43] Figure 4h presents the statistics information of V_{oc} values at different poling electric fields and temperatures, detail poling process and I-V shown in Figure S22 (Supporting Information). At each temperature, the device underwent poling for 16 s with varying electric fields, followed by I-V curve scans to measure V_{oc} . The results clearly indicate that at lower temperatures, the device exhibits lower V_{oc} values and requires more time to reach saturation, in line with the increased difficulty of ion migration at lower temperatures. Conversely, at higher temperatures, saturation occurs with lower time taken due to increased ion migration activity, resulting in higher V_{oc} values. These findings substantiate the origin of the switchable photovoltaic effect in perovskite lateral structure devices, driven by ion migration. $V_{\rm oc}$ variation over time also corroborates these trends. In Figure 4i, V_{oc} was continuously monitored under 10 mW cm⁻² illumination. At room temperature (298 K) and above, V_{oc} relaxed to the initial state (0 V) within ten minutes and eventually stabilized \approx -0.03 V, this slight deviation can be understood as interference from the test instrument or continuous lighting during the process. The significant difference lies in the considerably lower V_{oc} values at low temperatures under the same illumination and measurement conditions. Moreover, the V_{oc} values change more slowly over time and ultimately cannot return to the initial state in the cold environment. This observation indicates the greater difficulty of ion spontaneous rediffusion at lower temperatures, a characteristic vividly

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Figure 4. Light and temperature effect on SPV. a) Photoconductivity of the Ti/CsMAFA/Ti device read at 0.1 V, under red (623 nm), green (525 nm), and blue (445 nm) illuminations. b) *I–V* curves after different illuminations time. c) I_{sc} of lateral devices with different poling electric fields and light intensity. d) Photovoltaic characteristics with different light intensity (light wavelength: 623 nm). e) I_{sc} statistics with different wavelengths (445, 525, and 623 nm) and intensities (0.1–1.0 mW mm⁻²) of light. f) Poling (Dark) current of the Ti/Perovskite/Ti (20 µm) device under 0.3 V µm⁻¹ electric field with different temperature (from 123 to 348 k). g) The relationship of conductivity and temperature of the CsMAFA film under dark and illumination (623 nm, the light intensity is 50 mW cm²) h) V_{oc} values dependence of temperature for lateral devices, poled for 25 s. i) The V_{oc} retention time (illuminated at 10 mW cm⁻²) under different temperatures.

reflected in the $V_{\rm oc}$ relaxation behavior under low-temperature conditions.

2.5. SPV Mechanism Analysis

To further prove the mechanism of the SPV phenomenon and more directly observe the band bending caused by film doping, we executed KPFM for characterization of the lateral device with the top electrode structure. The top electrode with an electrode spacing of 100 μ m was evaporated on the surface of the perovskite film through a shadow mask. KPFM is a scanning probe technique, which detects the local surface potential by recording the surface potential change of the devices. **Figure 5**a and Figure S23 (Supporting Information) show the device structure in detail, the device connected to the power supply through wires to achieve

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Figure 5. Switchable photovoltaic mechanism analysis. a) Schematic image of KPFM analysis of the lateral device. b) KPFM potential image of the perovskite/Au interface before and c) after positive poling. The line graph reflects the potential change along the red line. Scanning area: $20 \,\mu\text{m} \times 20 \,\mu\text{m}$. d) Potential results after 10 V bias applied to the device. The electric potential gradually increases from bottom to top. The white arrows in (d) and (f) reflect the direction of the applied electric field for poling. The blue dot at the end of lines marking the starting points. e) KPFM surface potential images before poling. f) The potential of device after poling of -10 V bias, the potential change trend decreases from top to bottom.

biased. Before and after poling, KPFM was performed on the contact area between the electrode and the perovskite respectively, as shown in Figure 5b,c. The surface potential difference of the interface after poling is ≈ 0.2 V, lower than that (0.5 V) before poling. This shows that the redistribution of ions forms doping, which results in a change in potential difference, corresponding to the energy diagrams we proposed. Figures 5d-f show the surface potential of the perovskite film before and after poling. As the red line on the film, the potential fluctuation along the red line remains within 20 mV, suggesting there is an even distribution of space charges in the undoped film before poling (Figure 5e). After applying a constant 10 V bias (effective 0.1 V μm^{-1}) to the device, the potential changes are shown in Figure 5d, where the surface potential distribution gradually increases from bottom to top, indicating that p-doping occurs near the anode. Similarly, when a negative bias is applied to the device, the surface potential of the film changes in a consistent trend with the poling direction change. It is worth mentioning that in previous study exploring the photoluminescence effects, Cheng et al. developed a dynamic transport model accounting for the local electron and hole concentration change with the drift of vacancies.^[44] Notably, the movement of these vacancies is propelled by the applied bias, which further indicates that the ions migration and doping are caused by poling.

3. Conclusion

In summary, we systematically studied the effects of different factors on the SPV phenomenon, including poling conditions, electrode spacing, metal contact, lighting conditions, and temperature. More importantly, to date, there is no precise the ory to describe the ion migration mechanism and interface characteristics of LHP/electrode. Compared with previous reports on SPV, this study particularly emphasizes that different LHP/electrode contacts lead to different interface energy states or interface reactions, which have a significant impact on the

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LHP-based photovoltaic devices. Furthermore, these findings reveal how bias affects the lateral ion migration of perovskite film with different metal contact conditions. Contributing to the construction of durable and reliable perovskite-based optoelectronic devices and the understanding of their electrical mechanisms, such as SPV devices, memristors, transistors, and emerging synaptic devices.

4. Experimental Section

Lateral Electrode Fabrication: The lateral electrodes were fabricated on silicon (Si) wafers with a 300 nm silicon oxide (SiO₂). Before use, the wafer undergoes a sequence of cleansing procedures, commencing with Decon 90, followed by acetone, isopropyl alcohol, and deionized water. The wafer was soaked for 15 min in an ultrasonic bath for each cleaning step, followed by nitrogen drying. Photoresist (AZ 5214E) was spin-coated on the substrate at 4000 rpm and annealed at 105 °C for 2 min. Then, the electrode pattern was defined through the mask by UV light using a contact photolithography mask aligner (Karl Suss MJB 4). Next, development was done for 50 s in a solution of AZ developer and DI water (1:2). Ag and Au layers of 45 nm were deposited by thermal evaporation, with a 5-nm chromium layer deposited on bottom as an adhesion layer. Cr, Ti, and Pt metals of 50 nm were deposited by electron beam evaporation. ITO of 50 nm was deposited by magnetron sputtering. All these metal depositions were carried out in a high vacuum environment (< 2×10^{-6} mbar). Finally, the lift-off step was carried out in acetone with ultrasonic treatment for 5 min and the substrates cleaned with isopropyl alcohol.

Film Formation: Perovskite films were prepared using a two-step spincoating process within an argon (Ar)-filled glovebox. CsI (99.99% trace metals basis), MABr (GreatCell Solar), PbBr₂ (TCI, 99.99% trace metals basis), FAI (GreatCell Solar) and PbI₂ (TCI, 99.99% trace metals basis) were weighed and dissolved in a DMF-DMSO co-solvent (volume ratio of 4:1, DMF: Sigma-Aldrich, anhydrous 98.8%, DMSO: Sigma-Aldrich, anhydrous, \geq 99.9%) to form a 1.2 M Cs_{0.05}MA_{0.15}FA_{0.70}PbI_{2.5}Br_{0.5} precursor. The precursor solution was heated and stirred at 50 °C for 30 min to facilitate dissolution. Subsequently, the precursor was drop-cast onto the substrate, spun at 1000 rpm for 10 s, followed by 6000 rpm for 20 s. Chlorobenzene added in the 10th second before the end of spin-coating process. Finally, the sample was annealed at 100 °C for 1 h.

Device Measurements: Electrical measurements were carried out on a continuously pumped vacuum probe station, using a Keithley 4200 semiconductor analyzer to apply sweeping or constant voltage bias while measuring the current. Various intensity light was vertically illuminated onto the device through a quartz window on the probe station. Measurements at different temperatures were conducted on a cryogenic probe station, with the vacuum below 1×10^{-4} mbar. The sheet resistance is determined through the four-point probe method (CMT SR – 2000 N Semi-Automated Sheet Resistance and Resistivity Measurement System), measuring the resistance of the metal layer deposited uniformly across the entire substrate. All KPFM images were obtained using Cypher S AFM in the electric lift mode (Air and Dark). The lift-scan height was set to 100 nm, and the scanning rate was 1 Hz.

UPS and XPS Measurements: XPS and UPS was performed on Kratos AXIS supra with aluminum X-ray monochromatic and helium sources, respectively. The XPS region scan was performed with a step size of 0.1 eV with a 221.40 ms dwell time. UPS was measured from -3.78 to 21.22 eV with a 0.025 eV step size and 65.15 ms dwell time.

SEM Measurements: The SEM image of the perovskite film was obtained using field-effect scanning electron microscopy (FE-SEM, JEOL JSM-6340F).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

halide perovskites, ion migration, metal contacts, open circuit voltage, switchable photovoltaics

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