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Toward Switchable Photovoltaic Effect via Tailoring Mobile Oxygen Vacancies in Perovskite Oxide Films

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Supporting Information

ABSTRACT: The defect chemistry of perovskite oxides involves the cause to most of their abundant functional properties, including interface magnetism, charge transport, ionic exchange, and catalytic activity. The possibility to achieve dynamic control over oxygen anion vacancies offers a unique opportunity for the development of appealing switchable devices, which at present are commonly based on ferroelectric materials. Herein, we report the discovery of a switchable photovoltaic effect, that the sign of the open voltage and the short circuit current can be reversed by inverting the polarity of the applied field, upon electrically tailoring the distribution



of oxygen vacancies in perovskite oxide films. This phenomenon is demonstrated in lateral photovoltaic devices based on both ferroelectric $BiFeO_3$ and paraelectric $SrTiO_3$ films, under a reversed applied field whose magnitude is much smaller than the coercivity value of $BiFeO_3$. The migration of oxygen vacancies was directly observed by employing an advanced annular bright-field scanning transmission electron microscopy technique with in situ biasing equipment. We conclude that the band bending induced by the motion of oxygen vacancies is the driving force for the reversible switching between two photovoltaic states. The present work can provide an active path for the design of novel switchable photovoltaic devices with a wide range of transition metal oxides in terms of the ionic degrees of freedom.

KEYWORDS: switchable photovoltaic effect, oxygen vacancy, perovskite oxide films, ion drift, laser molecular beam epitaxy

INTRODUCTION

Energy harvesting by photovoltaic devices has received a considerable amount of attention over recent years due to the worldwide energy crisis.¹ Photovoltaic cells based on ferroelectric materials are regarded as one of the promising candidates for light-to-electricity energy conversion devices. In the ferroelectric photovoltaic effect, the separation of photogenerated electron-hole pairs relies on the spontaneous ferroelectric polarization originating from polar noncentrosymmetry.³ One outstanding feature of ferroelectric photovoltaic devices 4^{-26} is the switchable photovoltaic effect, i.e., that the direction of the photocurrent and the sign of the open-circuit voltage in these devices can be controlled by the applied bias. Previous investigations pertaining to the switchable photovoltaic effect in the ferroelectrics attributed this phenomenon to the ferroelectric polarization-induced band bending,^{4–16} the cooperative effect of polarization and oxygen vacancies,17-22 the Schottky-Ohmic conversion at the oxygen vacancies controlled interface,²³ and the domain wall theory.^{24–26}

Recent advances in discovering the giant switchable photovoltaic effect of organic–inorganic hybrid perovskite devices have enhanced the interest of research concerning the switchable photovoltaic phenomenon.^{27–29} Some investigations have demonstrated that the drift of $CH_3NH_3^+$ and Pb^{2+} cations or I[–] anions in organometal trihalide perovskite films can be triggered by applying an external electric field between two terminals, leading to a switchable photovoltaic effect with high photocurrent output.^{27–29} As a result, the switchable photovoltaic effect induced by mobile ions has been intensively studied in organic–inorganic hybrid perovskite materials.^{30,31}

Oxygen vacancies constitute an important functional ion defect in transition metal oxides.^{32–37} These oxide materials possess a wide range of work functions depending on the band filling controlled by the amount of oxygen vacancies.³⁶ It is well-known that the formation energies of charged oxygen

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Figure 1. (a) X-ray reciprocal space mapping taken around the (113) reflection for the 100 nm BFO films on the STO substrates. The dashed line indicates the position of the (113) STO reflection. (b) Schematic diagram of the lateral structure photovoltaic devices. Photocurrents of the pristine, positive poled, and negative poled photovoltaic devices based on BFO (c) and STO (d) films under the illumination of a 375 nm laser with a power density of ~900 mW/cm². The poling electric fields are $\pm 100 \text{ kV/cm}$ with 400 pulses. Here, the measurement conditions for both STO films and BFO films were exactly the same. All data are recorded at room temperature.

vacancies in many oxide materials are low.³⁸ Thus, oxygen vacancies are always present in oxide films even when their synthesis is performed under high oxygen pressure. Most importantly, the oxygen ions or vacancies are mobile in the presence of an electric field, according to the recent studies on the resistive switching phenomenon^{39,40} and to our in situ scanning transmission electron microscopy (STEM) measurements which will be presented later in this work. This feature makes the oxide materials potentially interesting in terms of ionic control of functional properties. As demonstrated recently, the integration of this ionic degrees of freedom into oxide devices can be exploited to actively manipulate electrical conduction,^{38,41} interface magnetism,⁴² and catalytic activity.^{35,43}

In this work, we propose a strategy to induce the switchable photovoltaic effect in functional perovskite oxide films by tailoring the distribution of mobile oxygen ions or vacancies upon applying an external electric field. We validate the proposed scenario by performing photovoltaic measurements on both multiferroic BiFeO₃ (BFO) with a relatively small bandgap of 2.71 eV (see Figure S1 in the Supporting Information, SI) and paraelectric SrTiO₃ (STO) with a bandgap of 3.2 eV. From detailed photovoltaic measurements and STEM characterization, we conclude that the band bending induced by the migration of oxygen vacancies is the main cause for the reversible switching between two photovoltaic states in both BFO and STO. The demonstration of the oxygenvacancy-controlled switchable photovoltaic effect opens the way to the design of novel optoelectronic devices based on perovskite oxides.

RESULTS AND DISCUSSION

BFO and STO thin films were grown on STO substrates in the same fabrication conditions using the laser molecular beam epitaxy (LMBE) technique (see Materials and Methods for more details), and the thickness of both BFO and STO films is 100 nm. We measured the (113) peak to carry out the structural analysis using a high-resolution reciprocal space mapping (RSM) technique (see Figure 1a). Our BFO film does not show any splitting of the (113) peak, implying that its unit cell is tetragonal.^{44,45} The BFO thin film with a thickness of 100 nm was grown coherently with the STO substrate, according to the fact that the (113) peak of the film has the same H as the (113) peak of the substrate. Hence, the in-plane lattice constant is the same as the STO substrates (3.905 Å). From the (113) peak position, we calculate the out-of-plane lattice constant to be 4.054 Å. The in-plane compressive strain induces a stretch in the out-of-plane direction. The obtained lattice parameters verify that the BFO film was epitaxially grown on the (001) STO substrate, and the phase of our BFO film can be described in terms of a tetragonal unit cell, in agreement with the recent investigations.44-4

In order to investigate the effects of the field-induced oxygen vacancy layer on the photovoltaic properties of these perovskite films, we fabricated the lateral photovoltaic devices and measured the photovoltaic effect in the BFO and STO films by applying the electric field at room temperature. The lateral photovoltaic architecture with a geometry symmetry was employed as our device structure (see Figure 1b). The photograph of our lateral device is shown in Figure S2, where the planar electrodes were patterned on our BFO and STO films with a thickness 100 nm. The direction of the photocurrent is parallel to the film plane for lateral photovoltaic



Figure 2. (a) The spectral dependence of the short-circuit current J_{sc} in the pristine and poled (+100 kV/cm, 1000 pulses) BFO devices. The inset shows a semilog illustration, and the dash line represents the band gap of BFO. (b) The J_{sc} as a function of time with 375 nm laser on and off in the positive and negative poled devices. Zero-bias open voltage V_{oc} (c) and photocurrent J_{sc} (d) with the repetition of bias polarity switching. (e) The dependence of open voltage V_{oc} and short-circuit current J_{sc} on the applied electric field. (f) The temperature dependence of photocurrent density versus voltage curves. The voltage pulses were applied at each temperature, and then J-V curves were measured. The arrow indicates the direction of increasing temperature.

structures, while it is perpendicular to the film plane for usual vertical structures.²⁷ In order to avoid the impact of a Schottky barrier at the interfaces and to capture a clear physical picture, we utilized chromium as a material for the electrodes. *N*-type BFO films with a work function of ~4.7 eV and STO films with a work function of ~5.2 eV can form ohmic contacts with chromium, whose work function is 4.5 eV.^{47–49} To exclude the contribution of ferroelectric polarization, the applied electric fields are below the coercivity value (>160 kV/cm) in our BFO films (see Figure S3). An ultraviolet laser with a wavelength of 375 nm was used on the lateral photovoltaic measurement. The light covers all the surfaces of the sample, to exclude the contribution of inhomogeneous illumination.^{50,51}

Figure 1c represents the switchable photovoltaic effect of the lateral BFO device. Symmetrical current–voltage (J-V) characteristics in the as-prepared BFO device show no photovoltaic effect with zero open circuit voltage ($V_{\rm oc}$). Interestingly, a $V_{\rm oc}$ of +150 mV and a short-circuit current density ($J_{\rm sc}$) of -67 μ A/cm² emerged in the BFO device after applying a positive bias of +100 kV/cm with 400 pulses (200

ms duration, 200 ms interval). The electric field pulses were employed to prevent sample heating. Correspondingly, by applying a negative bias of -100 kV/cm, the orientation of the photovoltaic direction $(V_{oc} \text{ and } J_{sc})$ is inverted compared with that resulting from a positive bias. The values of $V_{\rm oc}$ and $J_{\rm sc}$ under a negative bias were -150 mV and $+66 \mu$ A/cm², respectively. The direction of J_{sc} is always opposite to the bias direction, as can be seen from Figure 1c, which indicates that the direction of the built-in field is opposite to the bias direction. V_{oc} is independent of the light power, while J_{sc} increases linearly as a function of it (see Figure S4). The possibility to switch the polarity of the diode by applying an electric field without illumination further implies the existence of a field modulated band bending phenomenon in our devices (see Figure S5). While the conduction of the pristine device presents a symmetric feature, a forward diode is formed by applying a positive bias, and a diode with opposite polarity is formed by applying a negative bias. This result is consistent with the observed switchable photovoltaic effect.



Figure 3. HAADF (a) and ABF (b) micrographs of the pristine BFO/SNTO heterostructures. HAADF (c) and ABF (d) micrographs of the positive poled BFO/SNTO heterostructures by in situ applying voltage. The arrows indicate where the interface locates. The images were taken along the [110] pseudocubic direction. (e–h) ABF line profiles of the Fe—O—Fe chains with respect to the bars indicated in Figure 2d,f. The line profiles correspond to the bars with the same colors in the ABF images. The magenta/green circles display the O and Fe sites, respectively. The lighter magenta ones denote the presence of oxygen vacancies.

The STO films, fabricated under the same condition as the BFO films, also exhibit this switchable photovoltaic phenomenon after being polarized by external electric pulses (see Figure 1d). Similarly, the pristine STO lateral devices do not exhibit any photovoltaic effect. The values of V_{oc} and J_{sc} in the forward biased STO device were -140 mV and $+149 \mu \text{A/cm}^2$, respectively, while the same values in the presence of a negative bias were +160 mV and $-173 \ \mu \text{A/cm}^2$, respectively. The V_{oc} values of the BFO and STO devices are almost the same, demonstrating the dominant role of oxygen vacancies over that of polarization reversion in our BFO device. The J_{sc} value of STO with a bandgap 3.2 eV is almost three times as much as that of BFO with a bandgap 2.7 eV. This is ascribed to the difference of mobility between BFO and STO. The photovoltaic response in BFO is limited by the low carrier mobility,⁵⁵ while better photovoltaic performance in STO can be achieved due to a higher mobility compared with that of BFO.53 Nevertheless, we did not observe the switchable photovoltaic effect in STO single crystals after poling (see Figure S6), which suggests an essential role of the migration of oxygen vacancies in the devices. Moreover, this phenomenon rules out the possible role played by the STO substrate in the BFO/STO heterostructure. The contrasting behavior of our experiments between BFO and STO devices allows us to hypothesize that these phenomena originate from the voltage-driven motion of oxygen ions or vacancies in perovskite oxide films. The complete absence of photovoltaic effect in the pristine devices and the presence of a switchable photovoltaic effect in the polarized devices imply that built-in fields can be induced in the polarized perovskite oxide films.

The spectral dependence of the J_{sc} in the pristine and poled BFO devices also proves the appearance of a built-in field in the poled BFO device (see Figure 2a). No spectral response of the short-circuit current J_{sc} was observed in the pristine BFO device, as opposed to the poled BFO device (see Figure 2a), which is active in the spectral range from 500 to 700 nm, reflecting a sub-band gap feature ascribed to the existence of oxygen vacancies.⁵⁴ The trends of steady-state photocurrents as a function of time at zero bias after poling clearly demonstrate that the photocurrent can be switched ON and OFF repeatedly (see Figure 2a). Figure 2c,d displays that the V_{oc} can be reversed by alternately applying an electric field of ± 100 kV/cm in over 20 measuring sequences, which indicates good reversibility, and J_{sc} shows a similar behavior. The dependence of the photovoltaic effect on the poling electric field was also investigated. V_{oc} and J_{sc} increase almost linearly with the poling electric field (see Figure 2e). The photovoltaic effect occurs when the magnitude of the poling electric field is higher than 5 kV/cm, which indicates a threshold for the activation of oxygen vacancy migration under an external electric field.

Figure 2f represents the influence of temperature on the vacancy-dominated photovoltaic phenomena in our BFO devices. The electric pulses were applied at different temperatures, i.e. 20 °C, 100 °C, 200 °C, and 300 °C. Both V_{oc} and J_{sc} increase with the temperature. In fact, the V_{oc} value at 300 °C is three times as large as that at room temperature, and the J_{sc} value at 300 °C is 1 order of magnitude larger than that at room temperature. As a consequence, the power conversion efficiency at 300 °C is about 2 orders of magnitude higher than that at room temperature. However, larger leakage currents in BFO

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films at higher temperatures hamper the impact of the external electric field and pose a limit to the further improvement of photovoltaic performance, leading to a very similar photovoltaic behavior at 200 and 300 °C (see Figure 2f). This temperaturedependent behavior can further demonstrate the major role played by the migration of oxygen vacancies in our perovskite devices, because more oxygen vacancies can accumulate on one side as the ionic transport is favored by higher temperatures. Recent studies on the temperature dependence of the photovoltaic effect in a BFO/La_{2/3}Sr_{1/3}MnO₃ heterojunction have demonstrated that the V_{oc} decreases by ~50% and the J_{sc} increases by ~120% if the temperature rises 20 to 130 °C. The difference between these studies and our results can be explained by considering the different mechanisms which govern the photovoltaic performance in heterojunction type and in oxygen-vacancy-migration type devices.

To obtain a direct evidence of the field-induced migration of oxygen vacancies, which is of vital importance to understand the underlying mechanism, we employed an aberrationcorrected STEM technique with in situ biasing configuration. Recently, the advances in annular-bright-field (ABF) imaging have enabled the direct observation of light atoms such as oxygen,⁵⁶⁻⁵⁸ since the intensity contrast of ABF micrograph is proportional to $Z^{1/3}$, where Z is the atomic number. In our measurement, the 0.7 wt % Nb-doped STO (SNTO) substrate, which is highly conductive, acted as one electrode. A 65 nm thick Pt layer was sputtered onto the BFO film as the top electrode. The SNTO bottom electrode was always grounded, and a positive voltage of +1 V, corresponding to an electric field of $\sim +150$ kV/cm, was applied on the top electrode. A scheme of the experimental setup for the application of an electric field in STEM is shown in Figure S7.

Figure 3b illustrates the ABF image of the region at the pristine BFO/SNTO interface viewed along the [110] zone axis, which was recorded simultaneously with the high-angle annular dark-field (HAADF) image (see Figure 3a). The Bi sites are represented by the darker spots and the O sites are the lighter spots in the ABF image, while the Bi sites are represented by the lighter spots and the O sites are the darker spots in the HAADF image. Figure 3e,f presents the line profiles along the Fe-O-Fe chains marked by the blue and green bars in Figure 3b, respectively. Here, oxygen and iron ions are indicated by magenta and green circles, respectively. The deep valleys of the oxygen sites indicate small amounts of oxygen vacancies at the interface between BFO and SNTO. After acquiring these images, a + 1 V bias was applied in situ on the top electrode. The HAADF and corresponding ABF images of the poled BFO/SNTO heterostructure are shown in Figure 3c,d, respectively. Large amounts of oxygen vacancies, which can be seen in the line profiles of the ABF image, emerged at the interface. This is confirmed by the fact that the valleys of oxygen sites become shallower or even disappear (see Figure 3g,h). When a positive bias is applied to the top electrode, oxygen anions in BFO films are driven away from the interface between BFO and SNTO. In other words, the positively charged oxygen vacancies diffuse toward the BFO/SNTO interface. In addition, the shift of the Fe L_3 peak toward a lower energy, corresponding to the presence of a lower valence state in the Fe L-edge electron energy loss spectrum (EELS), also confirms the accumulation of oxygen vacancies at the BFO/ SNTO interface after applying a positive bias (see Figure S8), in agreement with ABF-STEM characterization results. Therefore, the in situ STEM measurements provide a direct observation of the drift of the oxygen vacancies along the direction of the applied electric field in BFO films.

From the results discussed above, we can conclude that the migration of oxygen vacancies can produce a switchable photovoltaic effect in perovskite oxides. In order to understand the physical process behind this switchable photovoltaic effect, the case of BFO will be discussed as an example. It is well-known that the incorporation of oxygen vacancies results in the formation of Fe^{2+} ions according to the available first-principle density functional calculations,⁵⁹ which gives rise to an impurity band in the bandgap and to an upward shift of the Fermi level (see Figure 4a,b). Hence, oxygen vacancies are commonly regarded as electron donors, each of which can supply one or two electrons.^{36,47} In the as-grown films, these vacancies are homogeneously distributed as sketched in Figure 4c. As a result, the band diagram of a metal/BFO/metal structure is sym-



Figure 4. Schematic diagrams of the electronic density of states in BiFeO₃ (a) and oxygen vacancy doped BiFeO_{3. δ} (b). Here, the dash dot lines indicate the Fermi level. The band filling is controlled via impurity band stemming from the oxygen vacancy induced Fe²⁺ ions. Schematic diagrams describing the distribution or redistribution of oxygen vacancies in the pristine (c), the positive poled (e), and the negative poled (g) BFO films. Oxygen vacancies are schematically drawn out as white dots. Blue color represents the region for BFO while red color denotes the region for oxygen vacancy doped BiFeO_{3. δ}. Corresponding schematic energy diagrams of the metal/BFO/metal structures consisting of the pristine (d), the positive poled (f), and the negative poled (h) BFO films. The dash dot lines indicate Fermi level. E_c denotes the bottom of the conduction band, and E_v represents the top of valence band.

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metrical (see Figure 4d), and no photovoltaic effect is expected. The oxygen ions or vacancies can be move when driven by an external electric field, as directly confirmed by our in situ STEM measurements. When an electric field is applied, the positive charged oxygen vacancies drift along the direction of the field, and thus accumulate near the negative electrodes, resulting in the creation of a highly *n*-type oxygen deficient layer in that region (see Figure 4e). This migration process breaks the intrinsic symmetry (see Figure 4e,g). Ultimately, this doping gradient arising from the inhomogeneous spatial distribution of oxygen vacancies leads to the formation of a built-in field, opposite to the direction of the applied field, in BFO films. Figure 4f depicts a scheme of the band diagram of the positive poled BFO film. The photovoltaic effect occurs with a negative short-circuit photocurrent (J_{sc}) and a positive open voltage $(V_{\rm oc})$, which explains the photovoltaic effect in the positive poled BFO device. If the direction of applied bias is reversed, the oxygen vacancies accumulate in the other electrode (see Figure 4g). This leads to the switching of the band diagram (see Figure 4h), which elucidates the mechanism behind the photovoltaic effect in the negative poled BFO device. As a consequence, this flipping of the band diagram is the reason behind the switchable functional properties.

CONCLUSIONS

We proposed a novel strategy to generate a switchable photovoltaic effect by tailoring the inhomogeneous spatial distribution of oxygen vacancies in perovskite oxide films with an external electric field. Using BFO and STO as our target materials, we demonstrated the switchable photovoltaic effect arising from the migration of oxygen vacancies using a lateral photovoltaic structure with geometry symmetry. The application of an electric field leads to the generation of a built-in field, whose direction can be manipulated, in perovskite oxide films. The field-induced drift of oxygen vacancies was directly confirmed by ABF-STEM imaging with in situ biasing. The devices based on this mechanism exhibit a photovoltaic performance which can be enhanced at high temperature. Here, we showed a pure bulk effect by designing symmetrical ohmic contacts, in order to distinguish the contribution of the Schottky interface.^{10,17,23} However, we would like to point out that the structures with Schottky interfaces exhibit a similar switchable photovoltaic effect, due to the oxygen vacancy migration-induced lowering of the Schottky barriers. Since this approach does not require ferroelectric materials, more transition metal oxides with small bandgaps can be employed to fabricate switchable photovoltaic devices with higher light absorption efficiency. The present work can open the way to the design of photovoltaic devices by employing ionic degrees of freedom in transition metal oxides.

MATERIALS AND METHODS

Epitaxial thin films BiFeO₃ (BFO) were grown on (00l) oriented SrTiO₃ (STO) and 0.7 wt % Nb doped SrTiO₃ (SNTO) substrates (MTI Ltd.) by laser molecular beam epitaxy (LMBE) technique using a XeCl excimer laser with a laser fluence of ~1.5 J/cm² and a repetition rate of 2 Hz. The growth was carried out under 10 Pa oxygen partial pressure. The growth temperature was kept 580 °C monitored by an infrared pyrometer. The films were annealed for 15 min then cooled down slowly to room temperature after growth. STO films were fabricated under the same condition with BFO. Film thickness was calibrated via both X-ray reflection (XRR) and transmission electron microscope (TEM).

High-resolution reciprocal-space mapping (RSM) were performed to investigate the crystal structure of the BFO thin films at the BL14B1 beamline of Shanghai Synchrotron Radiation Facility (SSRF), using a 1.24 Å X-ray with a Huber 5021 six-axis diffractometry. The RSM presented is plotted in reciprocal lattice units (r.l.u.) of the STO substrate (1 r.l.u. = $2\pi/3.905$ Å⁻¹).

TEM sample was prepared using the standard Focused Ion Beam (FIB) method and transferred to a *Nano-Chip*. The in situ electric field experiments were performed using a heating and bias DH30 holder produced by DENSsolutions Company. The atomic structures of the BFO films were characterized using an ARM–200CF (JEOL, Tokyo, Japan) STEM operated at 200 keV and equipped with double spherical aberration ($C_{\rm s}$) correctors (CEOS GmbH, Heidelberg, Germany). The attainable resolution is about 78 picometers.

To fabricate the lateral photovoltaic devices, we utilized the standard photolithography technique to define the coplanar interdigitated electrodes. Ten nm Cr and 40 nm Au were thermally deposited on the prepatterned photoresist layer in succession. Au was utilized to protect Cr from oxidation. Then, the devices were completed after the conventional lift-off process by acetone. The photocurrent curves were measured via a Keithley 4200 semiconductor parameter analyzer under the illumination of a continuous laser with wavelength of 375 nm (~1000 mW/cm²). The electrical pulses to avoid the heating effect were applied via a Keithley 4200 semiconductor parameter analyzer (200 ms duration, 200 ms interval). The electrode area equals the effective length of the interdigital electrode multiplied by the thickness of film. The spectral photocurrents were measured by employing a monochromator (Zolix Instruments) combined with a lock-in amplifier (Standford SR-380) and an optical chopper. A 150 W Xeon lamp (Zolix Instruments) was utilized as the light source. The light intensity was calibrated by measuring its spectral power distribution using a standard silicon photodetector.

The transmission spectra were measured using an UV-vis-NIR spectrometer at room temperature. The optical bandgap E_g can be calculated according to a Tauc plot following $\alpha E = A(E - E_g)^n$. Here, α is the absorption coefficient, E is the photon energy, and A is a constant. The parameter n = 1/2 stands for the direct bandgap, while n = 2 denotes the indirect bandgap. In our case, the clear linear dependence in the $(\alpha E)^2$ versus E curve reveals that the bandgap is direct, and the calculated direct bandgap is 2.71 eV.

The ferroelectric nature of the BFO films on Nb-doped STO substrates was characterized using Piezoelectric Force Microscopy (PFM) performed on a commercial atomic force microscope (AFM, Asylum Reasearch MFP-3D). PFM images were collected and recorded using a Ti/Ir-coated Si cantilever (Olympus Electrilever) with a nominal ~2 N/m spring constant and a free air resonance frequency of ~70 kHz.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b13203.

Transmittance spectra, photograph of lateral photovoltaic device, PFM phase image, intensity dependence of V_{oc} and J_{sc} , dark current, schematic diagram of in situ STEM measurement, and EELS data (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Polman, A.; Knight, M.; Garnett, E. C.; Ehrler, B.; Sinke, W. C. Photovoltaic Materials: Present Efficiencies and Future Challenges. *Science* **2016**, *352*, aad4424.

(2) Paillard, C.; Bai, X.; Infante, I. C.; Guennou, M.; Geneste, G.; Alexe, M.; Kreisel, J.; Dkhil, B. Photovoltaics with Ferroelectrics: Current Status and Beyond. *Adv. Mater.* **2016**, *28*, 5153–5168.

(3) Stuman, B. I.; Fridkin, V. M. *The Photovoltaic and Photorefractive Effects in Noncentrosymmetric Materials*; Gordon and Breach Science Publishers: London, 1992.

(4) Choi, T.; Lee, S.; Choi, Y.; Kiryukhin, V.; Cheong, S.-W. Switchable Ferroelectric Diode and Photovoltaic Effect in BiFeO₃. *Science* **2009**, *324*, 63–66.

(5) Grinberg, I.; West, D. V.; Torres, M.; Gou, G.; Stein, D. M.; Wu, L.; Chen, G.; Gallo, E. M.; Akbashev, A. R.; Davies, P. K.; Spanier, J. E.; Rappe, A. M. Perovskite Oxides for Visible-Light-Absorbing Ferroelectric and Photovoltaic Materials. *Nature* **2013**, *503*, 509–512.

(6) Nechache, R.; Harnagea, C.; Li, S.; Cardenas, L.; Huang, W.; Chakrabartty, J.; Rosei, F. Bandgap Tuning of Multiferroic Oxide Solar Cells. *Nat. Photonics* **2014**, *9*, 61–67.

(7) Nechache, R.; Harnagea, C.; Licoccia, S.; Traversa, E.; Ruediger, A.; Pignolet, A.; Rosei, F. Photovoltaic Properties of Bi₂FeCrO₆ Epitaxial Thin Films. *Appl. Phys. Lett.* **2011**, *98*, 202902.

(8) Chakrabartty, J.; Nechache, R.; Harnagea, C.; Rosei, F. Photovoltaic Effect in Multiphase Bi-Mn-O Thin Films. *Opt. Express* **2014**, *22*, A80–A89.

(9) Yang, S.; Martin, L.; Byrnes, S.; Conry, T.; Basu, S.; Paran, D.; Reichertz, L.; Ihlefeld, J.; Adamo, C.; Melville, A.; Chu, Y.; Yang, C.; Musfeldt, J.; Schlom, D.; Ager, J.; Ramesh, R. Photovoltaic Effects in BiFeO₃. *Appl. Phys. Lett.* **2009**, *95*, 062909.

(10) Ji, W.; Yao, K.; Liang, Y. C. Bulk Photovoltaic Effect at Visible Wavelength in Epitaxial Ferroelectric BiFeO₃ Thin Films. *Adv. Mater.* **2010**, *22*, 1763–1766.

(11) Han, H.; Song, S.; Lee, J. H.; Kim, K. J.; Kim, G.-W.; Park, T.; Jang, H. M. Switchable Photovoltaic Effects in Hexagonal Manganite Thin Films Having Narrow Band Gaps. *Chem. Mater.* **2015**, *27*, 7425–7432.

(12) Wang, F.; Grinberg, I.; Rappe, A. M. Band Gap Engineering Strategy via Polarization Rotation in Perovskite Ferroelectrics. *Appl. Phys. Lett.* **2014**, *104*, 152903.

(13) Young, S. M.; Zheng, F.; Rappe, A. M. First-Principles Calculation of The Bulk Photovoltaic Effect in Bismuth Ferrite. *Phys. Rev. Lett.* **2012**, *109*, 236601.

(14) Chen, B.; Li, M.; Liu, Y.; Zuo, Z.; Zhuge, F.; Zhan, Q.-F.; Li, R.-W. Effect of Top Electrodes on Photovoltaic Properties of Polycrystalline BiFeO₃ Based Thin Film Capacitors. *Nanotechnology* **2011**, *22*, 195201.

(15) Guo, R.; You, L.; Zhou, Y.; Lim, Z. S.; Zou, X.; Chen, L.; Ramesh, R.; Wang, J. Non-Volatile Memory Based on The Ferroelectric Photovoltaic Effect. *Nat. Commun.* **2013**, *4*, 1990.

(16) Lee, D.; Baek, S.; Kim, T.; Yoon, J.-G.; Folkman, C.; Eom, C.; Noh, T. Polarity Control of Carrier Injection at Ferroelectric/Metal Interfaces for Electrically Switchable Diode and Photovoltaic Effects. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2011**, *84*, 125305.

(17) Yi, H.; Choi, T.; Choi, S.; Oh, Y. S.; Cheong, S. W. Mechanism of The Switchable Photovoltaic Effect in Ferroelectric BiFeO₃. *Adv. Mater.* **2011**, *23*, 3403–3407.

(18) Matsuo, H.; Kitanaka, Y.; Inoue, R.; Noguchi, Y.; Miyayama, M. Cooperative Effect of Oxygen-Vacancy-Rich Layer and Ferroelectric Polarization on Photovoltaic Properties in BiFeO₃ Thin Film Capacitors. *Appl. Phys. Lett.* **2016**, *108*, 032901.

(19) Hu, W. J.; Wang, Z.; Yu, W.; Wu, T. Optically Controlled Electroresistance and Electrically Controlled Photovoltage in Ferroelectric Tunnel Junctions. *Nat. Commun.* **2016**, *7*, 10808.

(20) Xing, J.; Guo, E.-J.; Dong, J.; Hao, H.; Zheng, Z.; Zhao, C. High-Sensitive Switchable Photodetector Based on BiFeO₃ Film with In-Plane Polarization. *Appl. Phys. Lett.* **2015**, *106*, 033504.

(21) Guo, Y.; Guo, B.; Dong, W.; Li, H.; Liu, H. Evidence for Oxygen Vacancy or Ferroelectric Polarization Induced Switchable Diode and Photovoltaic Effects in BiFeO₃ Based Thin Films. *Nanotechnology* **2013**, *24*, 275201.

(22) Yang, M.; Bhatnagar, A.; Alexe, M. Electronic Origin and Tailoring of Photovoltaic Effect in BiFeO₃ Single Crystals. *Adv. Electron. Mater.* **2015**, *1*, 1500139.

(23) Moubah, R.; Rousseau, O.; Colson, D.; Artemenko, A.; Maglione, M.; Viret, M. Photoelectric Effects in Single Domain BiFeO₃ Crystals. *Adv. Funct. Mater.* **2012**, *22*, 4814–4818.

(24) Yang, S.; Seidel, J.; Byrnes, S.; Shafer, P.; Yang, C.-H.; Rossell, M.; Yu, P.; Chu, Y.-H.; Scott, J.; Ager, J.; Martin, L. W.; Ramesh, R. Above-Bandgap Voltages From Ferroelectric Photovoltaic Devices. *Nat. Nanotechnol.* **2010**, *5*, 143–147.

(25) Seidel, J.; Fu, D.; Yang, S.-Y.; Alarcón-Lladó, E.; Wu, J.; Ramesh, R.; Ager, J. W., III Efficient Photovoltaic Current Generation at Ferroelectric Domain Walls. *Phys. Rev. Lett.* **2011**, *107*, 126805.

(26) Bhatnagar, A.; Chaudhuri, A. R.; Kim, Y. H.; Hesse, D.; Alexe, M. Role of Domain Walls in The Abnormal Photovoltaic Effect in BiFeO₃. *Nat. Commun.* **2013**, *4*, 2835.

(27) Xiao, Z.; Yuan, Y.; Shao, Y.; Wang, Q.; Dong, Q.; Bi, C.; Sharma, P.; Gruverman, A.; Huang, J. Giant Switchable Photovoltaic Effect in Organometal Trihalide Perovskite Devices. *Nat. Mater.* **2014**, *14*, 193–198.

(28) Yuan, Y.; Chae, J.; Shao, Y.; Wang, Q.; Xiao, Z.; Centrone, A.; Huang, J. Photovoltaic Switching Mechanism in Lateral Structure Hybrid Perovskite Solar Cells. *Adv. Energy Mater.* **2015**, *5*, 1500615.

(29) Zhao, Y.; Liang, C.; Zhang, H.; Li, D.; Tian, D.; Li, G.; Jing, X.; Zhang, W.; Xiao, W.; Liu, Q.; Zhang, F.; He, Z. Anomalously Large Interface Charge in Polarity-Switchable Photovoltaic Devices: An Indication of Mobile Ions in Organic–Inorganic Halide Perovskites. *Energy Environ. Sci.* **2015**, *8*, 1256–1260.

(30) Stoumpos, C. C.; Kanatzidis, M. G. Halide Perovskites: Poor Man's High-Performance Semiconductors. *Adv. Mater.* 2016, 28, 5778.
(31) Yuan, Y.; Huang, J. Ion Migration in Organometal Trihalide

Perovskite and Its Impact on Photovoltaic Efficiency and Stability. *Acc. Chem. Res.* **2016**, *49*, 286–293.

(32) Kalinin, S. V.; Spaldin, N. A. Functional Ion Defects in Transition Metal Oxides. *Science* **2013**, *341*, 858–859.

(33) Kalinin, S. V.; Borisevich, A.; Fong, D. Beyond condensed matter physics on the nanoscale: The Role of Ionic and Electrochemical Phenomena in The Physical Functionalities of Oxide Materials. *ACS Nano* **2012**, *6*, 10423–10437.

(34) Jang, H.; Kerr, G.; Lim, J.; Yang, C.-H.; Kao, C.-C.; Lee, J.-S. Orbital Reconstruction in A Self-Assembled Oxygen Vacancy Nanostructure. *Sci. Rep.* **2015**, *5*, 2045–2322.

(35) Jeen, H.; Choi, W. S.; Biegalski, M. D.; Folkman, C. M.; Tung, I.-C.; Fong, D. D.; Freeland, J. W.; Shin, D.; Ohta, H.; Chisholm, M. F.; Lee, H. Reversible Redox Reactions in An Epitaxially Stabilized $SrCoO_x$ Oxygen Sponge. *Nat. Mater.* **2013**, *12*, 1057–1063.

(36) Greiner, M. T.; Chai, L.; Helander, M. G.; Tang, W. M.; Lu, Z. H. Transition Metal Oxide Work Functions: The Influence of Cation Oxidation State and Oxygen Vacancies. *Adv. Funct. Mater.* **2012**, *22*, 4557–4568.

(37) Jin, K.; Li, Y.; Wang, Z.; Peng, H.; Lin, W.; Kyaw, A.; Jin, Y.; Jin, K.; Sun, X.; Soci, C.; Wu, T. Tunable Photovoltaic Effect and Solar Cell Performance of Self-Doped Perovskite SrTiO₃. *AIP Adv.* **2012**, *2*, 042131.

ACS Applied Materials & Interfaces

(38) Qin, Q. H.; Äkäslompolo, L.; Tuomisto, N.; Yao, L.; Majumdar, S.; Vijayakumar, J.; Casiraghi, A.; Inkinen, S.; Chen, B.; Zugarramurdi, A.; Puska, M.; van Dijken, S. Resistive Switching in All-Oxide Ferroelectric Tunnel Junctions with Ionic Interfaces. *Adv. Mater.* **2016**, *28*, 6852–6859.

(39) Waser, R.; Aono, M. Nanoionics-Based Resistive Switching Memories. *Nat. Mater.* **2007**, *6*, 833–840.

(40) Sawa, A. Resistive Switching in Transition Metal Oxides. *Mater. Today* **2008**, *11*, 28–36.

(41) Veal, B.; Kim, S.; Zapol, P.; Iddir, H.; Baldo, P.; Eastman, J. Interfacial Control of Oxygen Vacancy Doping and Electrical Conduction in Thin Film Oxide Heterostructures. *Nat. Commun.* **2016**, *7*, 11892.

(42) Bauer, U.; Yao, L.; Tan, A. J.; Agrawal, P.; Emori, S.; Tuller, H. L.; Van Dijken, S.; Beach, G. S. Magneto-Ionic Control of Interfacial Magnetism. *Nat. Mater.* **2014**, *14*, 174–181.

(43) Zhang, K.; Sushko, P.; Colby, R.; Du, Y.; Bowden, M. E.; Chambers, S. A. Reversible Nano-Structuring of $SrCrO_{3.\delta}$ Through Oxidation and Reduction at Low Temperature. *Nat. Commun.* **2014**, *5*, 4669.

(44) Guo, H.; Zhao, R.; Jin, K.-j.; Gu, L.; Xiao, D.; Yang, Z.; Li, X.; Wang, L.; He, X.; Gu, J.; Wan, Q.; Wang, C.; Lu, H.; Ge, C.; He, M.; Yang, G. Interfacial-Strain-Induced Structural and Polarization Evolutions in Epitaxial Multiferroic BiFeO₃ (001) Thin Films. ACS Appl. Mater. Interfaces **2015**, *7*, 2944–2951.

(45) Seidel, J.; Luo, W.; Suresha, S.; Nguyen, P.-K.; Lee, A.; Kim, S.-Y.; Yang, C.-H.; Pennycook, S. J.; Pantelides, S. T.; Scott, J.; Ramesh, R. Prominent Electrochromism Through Vacancy-Order Melting in A Complex Oxide. *Nat. Commun.* **2012**, *3*, 799.

(46) Liu, H.; Yang, P.; Yao, K.; Wang, J. Growth Rate Induced Monoclinic to Tetragonal Phase Transition in Epitaxial BiFeO₃ (001) Thin Films. *Appl. Phys. Lett.* **2011**, *98*, 102902.

(47) Wang, C.; Jin, K.-j.; Xu, Z.-t.; Wang, L.; Ge, C.; Lu, H.-b.; Guo, H.-z.; He, M.; Yang, G.-z. Switchable Diode Effect and Ferroelectric Resistive Switching in Epitaxial BiFeO₃ Thin Films. *Appl. Phys. Lett.* **2011**, *98*, 192901.

(48) Ge, C.; Jin, K.-J.; Wang, C.; Lu, H.-B.; Wang, C.; Yang, G.-Z. Numerical Investigation into The Switchable Diode Effect in Metal-Ferroelectric-Metal Structures. *Appl. Phys. Lett.* **2011**, *99*, 063509.

(49) Modak, B.; Ghosh, S. K. Origin of Enhanced Visible Light Driven Water Splitting by (Rh, Sb)-SrTiO₃. *Phys. Chem. Chem. Phys.* **2015**, 17, 15274–15283.

(50) Liao, L.; Jin, K.-j.; Ge, C.; Hu, C.-l.; Lu, H.-b.; Yang, G.-z. A Theoretical Study on the Dynamic Process of the Lateral Photovoltage in Perovskite Oxide Heterostructures. *Appl. Phys. Lett.* **2010**, *96*, 062116.

(51) Wang, S.; Wang, W.; Zou, L.; Zhang, X.; Cai, J.; Sun, Z.; Shen, B.; Sun, J. Magnetic Tuning of the Photovoltaic Effect in Silicon-Based Schottky Junctions. *Adv. Mater.* **2014**, *26*, 8059–8064.

(52) Wang, L.; Ma, H.; Chang, L.; Ma, C.; Yuan, G.; Wang, J.; Wu, T. Ferroelectric $BiFeO_3$ as an Oxide Dye in Highly Tunable Mesoporous All-Oxide Photovoltaic Heterojunctions. *Small* **2016**, DOI: 10.1002/smll.201602355.

(53) Son, J.; Moetakef, P.; Jalan, B.; Bierwagen, O.; Wright, N. J.; Engel-Herbert, R.; Stemmer, S. Epitaxial SrTiO₃ Films With Electron Mobilities Exceeding 30,000 cm2 V-1 S-1. *Nat. Mater.* **2010**, *9*, 482–484.

(54) Sung, J. H.; Lee, W.-M.; Lee, J. H.; Chu, K.; Lee, D.; Moya, X.; Mathur, N. D.; Yang, C.-H.; Park, J.-H.; Jo, M.-H. Single Ferroelectric-Domain Photovoltaic Switch Based on Lateral BiFeO₃ Cells. *NPG Asia Mater.* **2013**, *5*, e38.

(55) Yang, Y.; Xu, W.; Xu, X.; Wang, Y.; Yuan, G.; Wang, Y.; Liu, Z. The Enhanced Photocurrent of Epitaxial $BiFeO_3$ Film at 130° C. J. Appl. Phys. **2016**, 119, 044102.

(56) Guo, H.; Wang, J. o.; He, X.; Yang, Z.; Zhang, Q.; Jin, K. j.; Ge, C.; Zhao, R.; Gu, L.; Feng, Y.; Zhou, W.; Li, X. L.; Wan, Q.; He, M.; Hong, C.; Guo, Z.; Wang, C.; Lu, H.; Ibrahim, K.; Meng, S.; Yang, H.; Yang, G. The Origin of Oxygen Vacancies Controlling La_{2/3}Sr_{1/3}MnO₃

Electronic and Magnetic Properties. Adv. Mater. Interfaces 2016, 3, 1500753.

(57) Ge, C.; Jin, K. J.; Gu, L.; Peng, L. C.; Hu, Y. S.; Guo, H. Z.; Shi, H. F.; Li, J. K.; Wang, J. O.; Guo, X. X.; Wang, C.; He, M.; Lu, H.-B.; Yang, G.-Z. Metal–Insulator Transition Induced by Oxygen Vacancies from Electrochemical Reaction in Ionic Liquid-Gated Manganite Films. *Adv. Mater. Interfaces* **2015**, *2*, 1500407.

(58) Xu, Z. t.; Jin, K. j.; Gu, L.; Jin, Y. l.; Ge, C.; Wang, C.; Guo, H. z.; Lu, H. b.; Zhao, R. q.; Yang, G. z. Evidence for A Crucial Role Played by Oxygen Vacancies in LaMnO₃ Resistive Switching Memories. *Small* **2012**, *8*, 1279–1284.

(59) Ederer, C.; Spaldin, N. A. Influence of Strain and Oxygen Vacancies on The Magnetoelectric Properties of Multiferroic Bismuth Ferrite. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2005**, *71*, 224103.