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Oxygen-Valve Formed in Cobaltite-Based Heterostructures by Ionic Liquid and Ferroelectric Dual-Gating

Youdi Gu,^{†,‡,∇} Kun Xu,^{§,||,∇} Cheng Song,^{*,‡}[®] Xiaoyan Zhong,[§] Hongrui Zhang,[⊥] Haijun Mao,[#] Muhammad Shahrukh Saleem,[‡] Jirong Sun,[⊥][®] Wei Liu,^{*,†} Zhidong Zhang,[†] Feng Pan,[‡] and Jing Zhu[§][®]

[†]Shenyang National Laboratory for Materials Science, Institute of Metal Research, University of Chinese Academy of Sciences, Chinese Academy of Sciences, Shenyang 110016, China

[‡]Key Laboratory of Advanced Materials (MOE), School of Materials Science and Engineering, [§]National Center for Electron Microscopy in Beijing, Key Laboratory of Advanced Materials (MOE), The State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, and ^{II}Central for Nano & Micro Mechanism, Tsinghua University, Beijing 100084, China

¹Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, University of Chinese Academy of Science, Chinese Academy of Sciences, Beijing 100190, China

[#]College of Aerospace Science and Engineering, National University of Defense Technology, Changsha 410073, China

Supporting Information

ABSTRACT: Manipulation of oxygen vacancies via electric-field-controlled ionic liquid gating has been reported in many model systems within the emergent fields of oxide electronics and iontronics. It is then significant to investigate the oxygen vacancy formation/annihilation and migration across an additional ferroelectric layer with ionic liquid gating. Here, we report that via a combination of ionic liquid and ferroelectric gating, the remote control of oxygen vacancies and magnetic phase transition can be achieved in SrCoO_{2.5} films capped with an ultrathin ferroelectric BaTiO₃ layer at room



temperature. The ultrathin BaTiO₃ layer acts as an atomic oxygen valve and is semitransparent to oxygen-ion transport due to the competing interaction between vertical electron tunneling and ferroelectric polarization plus surface electrochemical changes in itself, thus resulting in the striking emergence of new mixed-phase SrCoO_x. The lateral coexistence of brownmillerite phase $SrCoO_{2.5}$ and perovskite phase $SrCoO_{3-\delta}$ was directly observed by transmission electron microscopy. Besides the fundamental significance of long-range interaction in ionic liquid gating, the ability to control the flow of oxygen ions across the heterointerface by the oxygen valve provides a new approach on the atomic scale for designing multistate memories, sensors, and solid-oxide fuel cells.

KEYWORDS: ionic liquid gating, ferroelectric polarization, oxygen vacancies, phase transition, oxygen valve

■ INTRODUCTION

Conventional valves, which control the direction, pressure, and flow of a fluid (liquid, gas, powder) in a fluid system on a macroscale, provide a fundamental role in our daily life. In most electronic devices, the control of charge flow is one of the most critical factors for the performance of integrated circuits.^{1,2} A typical application of controlling a one-way current flow is to fabricate a p-n junction between p-type and n-type materials in microelectronics. Many pivotal functionalities are based on such artificial control charge flow and are at the core of advanced microelectronics, logic circuits, and sensors, including rectification, amplification, resistance switching, and information storage.^{3,4} Nevertheless, with the urgent requirement for miniaturization and low power cost of the devices in the semiconductor industry, designing an atomicscale and voltage-actuated valve for controlling charge flow and electrical behavior is quite important and essential in electronic devices.

Oxygen vacancies have profound effects on crystalline structure evolution and property optimization of transitionmetal oxides (TMOs). Many of the functionalities of TMOs, such as in information storage,^{4,5} energy conversion,⁶ oxygen permeability,⁷ catalytic activity,^{8,9} etc., are controlled by the concentration and dynamics of oxygen vacancies. Especially, the natural oxygen sponge material of strontium cobaltite, denoted as SCO, the topotactic structural phase transition from brownmillerite SrCoO_{2.5} (B-SCO) to perovskite $SrCoO_{3-\delta}$ (0 $\leq \delta \leq$ 0.25, P-SCO), and concurrent changes in magnetic and electrical properties are all directly dominated by oxygen vacancies, which currently attracts much attention.⁸⁻¹³ Recently, oxygen vacancies in the SCO single layer have been widely explored by modifying oxygen background pressure^{9,10} and epitaxial strain.^{14,15} However, switching the environment between different oxygen pressures is still not so feasible for practical device application. Dynamic oxygen vacancy transport information is also missing. Since the

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epitaxial strain must be introduced during the sample preparation, and the oxygen vacancy content and transport information cannot be changed once the sample is put into use. Alternatively, manipulating the oxygen vacancy behavior via electric-field-controlled ionic liquid gating (ILG) in TMOs is of great interest for its high-density and low-power-cost applications.^{5,11,12} ILG utilizes the electric double layer (EDL) that forms at the liquid-solid interfaces to generate a much higher electric field on the sample surface that can bring about electrostatic carrier injection, migration of oxygen and hydrogen, and/or structural changes in the channel oxide materials.^{5,11,12,16-23} Although the electric-field-controlled oxygen and even hydrogen migration as well as tristate phase transformation have been reported in SCO thin films,¹¹ the formation and migration of oxygen vacancy across the adjacent chemically inert layer, e.g., ferroelectric (FE) materials, under an electric field has not been explored so far. Meanwhile, the selective manipulation of phase transitions between the brownmillerite and perovskite phases in SCO/FE multiferroic heterostructure by using FE polarization switching to adjust the energy barriers²⁴ can allow us to reveal the competition, coexistence, and cooperation of different crystal structures, as well as interplay among distinct properties. Such control can also lead to broad low-power consumption device applications, such as multistate memories and sensors.

In this study, we report a facile approach to control the oxygen vacancy formation/annihilation and transport in SCO thin films during electric-field-controlled ILG experiments via inserting the insulating BaTiO₃ (BTO) or SrTiO₃ (STO) separation layers between the functional layer and electrolyte. We found that the oxygen vacancies and topotactic phase transition can be remotely modulated at room temperature in SCO capped with various thicknesses of insulating BTO and STO layers. Moreover, compared with the same thickness of the dielectric STO layer, the ultrathin FE BTO layer in an appropriate thickness scale acts an atomic oxygen valve, which is semitransparent to oxygen vacancy/ions transport due to the competing interaction between electron tunneling and FE polarization plus surface electrochemical changes (oxygen ions migration) in BTO itself. This peculiar valve-controlled functionality directly results in the mixed-phase (M-SCO) film consisting of transversely arranged B-SCO phase and P-SCO phase but possessing different magnetic and electrical properties than either of the two phases. Thus, our results coin the concept of the "oxygen valve" to develop novel iontronic and electronic devices for novel energy and storage applications.

RESULTS AND DISCUSSION

Heterostructures of BTO/SCO and STO/SCO were grown on (001)-oriented STO substrates by pulsed laser deposition (PLD) method with in situ reflection high-energy electron diffraction (RHEED) monitoring (see the Methods and Figure S1, Supporting Information). Figure 1a shows the typical RHEED intensity oscillations during the deposition of 4 nm (10 unit cells) BTO layers after ~18 nm SCO grown on the STO substrate, indicating the layer-by-layer epitaxial growth of the BTO films. It is noted that the high-quality growth of SCO films is a prerequisite for ensuing layer-by-layer growth of BTO films. The initial sharp RHEED peaks at 0 s and final strip RHEED patterns at 224 s in the inset of Figure 1a can be clearly seen, suggesting the high crystal quality of the SCO and BTO films. The FE switching could be observed in the



Figure 1. (a) RHEED intensity oscillations during the deposition of a 4 nm (10 unit cells) BTO film on B-SCO (18 nm)/STO, with the insets showing the initial RHEED pattern at 0 s and the final diffraction strips at 224 s. (b) Typical out-of-plane PFM phase image recorded after applying to an outside $5 \times 5 \,\mu\text{m}^2$ area +6 V voltage and a smaller $3 \times 3 \,\mu\text{m}^2$ area with -6 V voltage then a further smaller $1 \times$ $1 \,\mu\text{m}^2$ area with +6 V voltage. (c) A cross-sectional low-magnification high-resolution high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image of BTO(4 nm)/B-SCO(18 nm) heterostructure, recorded along the [100] STO direction. The horizontal white dashed line denotes the interface of BTO/B-SCO. (d) An enlarged HAADF-STEM image from the red box of (c) showing the displacement direction of the Ti atoms in the BTO layer. The spontaneous polarization P_S direction of BTO, which is the same as δ_{Ti} is marked by vertical arrows. The horizontal white arrows denote the interface of BTO/B-SCO.

heterostructure with an ultrathin BTO of 4 nm, as shown in the piezoresponse force microscopy (PFM) out-of-plane image in Figure 1b. For the PFM measurements, the same ~18 nm SCO was deposited on a 0.7% Nb-doped (001) STO substrate as the bottom electrode to do the polarization switching. After writing an outside 5 \times 5 μ m² area with +6 V direct current (d.c.) bias, the PFM phase image of the BTO film shows a bright contrast, whereas after applying a negative d.c. bias of -6 V to a smaller 3 \times 3 μ m² area at the same location, the PFM phase image exhibits a dark contrast. The image contrast changes back to bright again after a positive d.c. bias of 6 V was applied to a further smaller $1 \times 1 \ \mu m^2$ area, which reveals a 180° FE switching of ultrathin BTO films. The FE nature of the 4 nm BTO thin film was further supported by the local piezoelectric hysteresis and butterfly amplitude loops (Figure S2, Supporting Information).^{25,26} Note that the SCO layer has a certain conductivity by adjusting the growth process (see the Methods) and thus can also directly serve as the bottom electrode to do the PFM measurements of BTO film. Similar FE properties were also observed in an 8 nm BTO film on SCO(18 nm)/STO(001) (Figure S2, Supporting Information).

To get further information about the growth mode and interface structure of BTO/B-SCO heterostructure, we performed the atomic resolution aberration-corrected high-

angle annular dark field scanning transmission electron microscopy (HAADF-STEM) analysis along [100] STO direction, as presented in Figure 1c,d. Coherent growth of a 4 nm BTO on an ~18 nm B-SCO film on STO(001) with an atomically flat and sharp BTO/B-SCO interface is presented in the low-magnification high-resolution HAADF-STEM image (Figure 1c). The high-density periodic dark strips parallel to the interfaces inside B-SCO film are discernible, implying the oxygen vacancy ordering superstructure feature of B-SCO. This is due to the alternate stacking of fully oxygenated CoO_6 octahedral and oxygen-deficient CoO₄ tetrahedral sublayers. To further demonstrate the ion displacement inside BTO, an enlarged HAADF-STEM pattern corresponding to the red outlined rectangle area in Figure 1c is shown in Figure 1d. The white arrows denote the BTO/B-SCO interface. Remarkably, the Ti ions are moved upward inside TiO₆ octahedrons of BTO, marked by the purple arrow. Identical to the direction of Ti-ion displacement, the direction of the spontaneous polarization (P_s) vector in BTO film is upward. This selfpoling behavior is in agreement with previous studies^{25,26} and usually attributed to the built-in electric field.^{26,27}

Such an FE displacement of Ti ions in BTO would have a direct and crucial valve effect on the electric field applied on the heterostructures through ILG. To clarify this influence, apart from the BTO(t)/B-SCO(18 nm) samples, we prepare B-SCO single layer and STO(t)/B-SCO (18 nm) bilayers (t =1.6, 2.4, 3.2, 4, 8, and 20 nm) for comparison and use N.Ndiethyl-N-(2-methoxyethyl)-N-methylammonium bis-(trifluoromethylsulfonyl)imide (DEME-TFSI) IL as the electrolyte to apply gate voltages. STO was chosen taking its comparable properties to BTO excepting ferroelectricity into account. In addition, both perovskites of STO and BTO have very similar band structures. The band gaps of the two are the same, 3.2 eV, and their electron affinity is \sim 4.0 and \sim 3.9 eV for BTO and STO, respectively.²⁸ Thus, STO is an ideal reference sample to study the role of FE polarization in the electric-fieldcontrolled oxygen vacancy transport experiments by ILG. We first investigate the effect of gate voltages on crystal structure of BTO/B-SCO and STO/B-SCO heterostructures using X-ray diffraction (XRD), as shown in Figure 2. A 5 mm scaled film was used for the XRD measurements. The whole area of the films is gated by the IL, and the nonvolatile nature of the ILG effect guarantees the feasibility of the ex situ experiments after removing the gate voltages.^{5,11,12} This nonvolatile feature also makes all of our subsequent ex situ studies possible and provides a wide range of applications. It is noted that the Co³⁺ ions are energetically stable in B-SCO phase compared with the unstable Co⁴⁺ ions in P-SCO phase. Meanwhile, B-SCO possesses well-ordered oxygen-vacancy channels and multivalent cobalt ions, which provide favorable conditions for ionic diffusion, valence state change, and final phase transition. Hence, we select the B-SCO phase as the initial state. Also, negative gate voltages are applied utilizing IL to address the topotactic phase transition between the B-SCO and P-SCO phases and associated interesting phenomena, thus simply and directly reflecting the oxygen ions' transport ability of SCO/FE heterostructures under an electric field.

The original crystal structure (0 V) of all BTO(t)/B-SCO heterostructures with the different BTO capping thicknesses clearly exhibits a characteristic doubling of the c axis lattice constant with the emergence of periodic half-order peaks of (002), (006), and (00<u>10</u>), originating from the alternate stacking of octahedral and tetrahedral sublayers along the c axis





Figure 2. (a) $\theta - 2\theta$ XRD spectra of 1.6, 2.4, 3.2, 4, 8, and 20 nm thick BTO films deposited on the 18 nm B-SCO/STO(001) after -6 V voltage is applied through ILG. As-grown bare 18 nm B-SCO and P-SCO films on STO(001) are also included as a reference. (b) Schematic crystal structures of BTO/M-SCO/STO(001) and BTO/B-SCO/STO(001) heterostructures. (c) $\theta - 2\theta$ XRD spectra of 1.6, 2.4, 3.2, 4, 8, and 20 nm thick STO films deposited on 18 nm B-SCO/STO(001) after a -6 V voltage is applied through ILG. As-grown bare 18 nm B-SCO and P-SCO films on STO(001) are also included as a reference. (d) Schematic crystal structures of STO/P-SCO and STO/B-SCO heterostructures grown on STO(001).

in the B-SCO layer (Figure S3a, Supporting Information). The diffractions of B-SCO(004) and (008) are, respectively, submerged in the (001) and (002) diffractions of the STO substrates owing to their closed lattice parameters $(1/4c_{B-SCO} =$ 3.9363 Å). The epitaxial BTO peaks (marked by asterisks) around the STO(001) and (002) peaks can also be caught in some samples with the thicker FE BTO capping layers (e.g., t =3.2, 4, 8, and 20 nm) (Figure S3a, Supporting Information). Figure 2a illustrates θ -2 θ XRD spectra of 1.6, 2.4, 3.2, 4, 8, and 20 nm thick BTO films deposited on the 18 nm B-SCO/ STO(001) after a -6 V voltage is applied for 40 min at room temperature through ILG. As-grown bare 18 nm B-SCO and P-SCO films on STO(001) are also included as a reference. The gating voltages and time are selected on the basis of our previous work¹² and a systematic analysis of phase transition with different voltages, thus ensuring the sufficiency of modulation. In addition, by monitoring the elapsed time dependence of the gate current (I_G) , we understood that the steady state can be reached in 40 min in our ILG experiments (Figure S4, Supporting Information). After gating, for the BTO(t)/B-SCO heterostructures with t = 1.6 and 2.4 nm, the characteristic half-order (002), (006), (0010), and (0014) peaks of the B-SCO phase (marked by dashed rectangles in Figure 2a) disappear and the buried SCO layers are totally transformed to P-SCO phase with the characteristic (002)

diffraction peaks of the P-SCO phase at about 47.8° (marked by diamonds in Figure 2a). This reflects that the negative gate voltage extracts the oxygen vacancies (or injects the oxygen ions) in the B-SCO layer across the ultrathin BTO layers (1.6–2.4 nm) by ILG and drives the phase transition, which is consistent with the gating results of the single B-SCO layer (Figure S5a, Supporting Information) and previous works.^{11,12}

The scenario differs dramatically for heterostructures with t= 3.2 and 4 nm. Apart from the new P-SCO(002) peak evolving on the right side of the STO(002) substrate peak in the θ -2 θ scans of Figure 2a, all of the half-order peaks of B-SCO phase are still present in those samples. The weak BTO peaks (marked by asterisks in Figure 2a) in those samples are also visible. It is noted that we have used a batch of samples to confirm this phenomenon. Also, the side effect of insufficient modulation is also excluded by our controlled experiments with different gating times and voltages (Figure S5, Supporting Information). These results undoubtedly indicate that the partial conversion of the B-SCO phase to the P-SCO phase in the buried SCO layer and emergence of a new mixed-phase $SrCoO_r$ (M-SCO) in the films are achieved by inserting ultrathin FE BTO layers (3.2-4 nm) in electric-fieldcontrolled ILG experiments. Recalling the PFM result in Figure 1b, obviously, FE polarization applies an energy barrier for oxygen vacancy migration and acts an atomic oxygen valve that is semitransparent to oxygen-ion transport. So the main feature for the phase transition here is from BTO/B-SCO to BTO/M-SCO, which is schematically highlighted by the crystal structures in Figure 2b. As t increases further to 8 and 20 nm, the buried B-SCO layers can no longer be converted to M-SCO or P-SCO phase. This is attributed to the greatly suppressed electric-field strength due to the enhanced BTO thickness and resultant FE polarization. Remarkably, our result is consistent with the gating effect in IL/BTO(8 nm)/ $La_{0.5}Sr_{0.5}MnO_3~(20~nm)^{22}$ and $IL/PbZr_{0.2}Ti_{0.8}O_3(8~nm)/La_{0.8}Sr_{0.2}MnO_3~(12~nm)^{23}$ systems. They both reported that the 8 nm thick FE layer is an effective buffer to reduce ion migration and allows access to pure electrostatic effects.

The STO(t)/B-SCO heterostructures respond differently to negative gate voltage from BTO(t)/B-SCO. Figure 2c displays θ -2 θ XRD spectra of t = 1.6, 2.4, 3.2, 4, 8, and 20 nm thick STO films deposited on the 18 nm B-SCO/STO(001) under the same gating time and biases as BTO capping at room temperature through ILG. For the STO(t)/B-SCO heterostructures, all buried B-SCO layers are successfully transformed to P-SCO phase when t is in the range of 1.6-8 nm, with the characteristic P-SCO(002) diffraction peaks at about 47.8° (marked by diamonds in Figure 2c). There are no half-order peaks in those samples. The main feature for the phase transition here is from STO/B-SCO to STO/P-SCO, which is schematically shown in Figure 2d. The results show that by extracting the oxygen vacancies (or injecting the oxygen ions) into the buried B-SCO layer, the phase transition of the SCO layer can be remotely driven across the 8 nm thick STO layer. The significant modulating difference between STO and BTO capping layers within 3.2-8 nm thickness in SCO-based heterostructures strongly emphasizes the important role of FE polarization for controlling oxygen vacancy migration. Similarly, the buried B-SCO layers can no longer be transformed into P-SCO phase as t increases to 20 nm. They exhibit the same prominent half-order peaks as the original STO(t)/B-SCO heterostructures (0 V, Figure S3b, Supporting) Information).

To confirm the three structurally distinct phases as mentioned above, the in-plane and out-of-plane strain states and structural parameters of typical B-SCO-, M-SCO-, and P-SCO-based films are characterized by using X-ray reciprocal space mappings (RSMs), as presented in Figure 3. RSM is a



Figure 3. X-ray RSMs from (a) B-SCO(18 nm)/STO(001), (b) BTO(3.2 nm)/M-SCO(18 nm)/STO(001), and (c) STO(3.2 nm)/P-SCO(18 nm)/STO(001) heterostructures around the ($\overline{1}03$) Bragg reflection of the STO substrates.

powerful method to quantify the strain state, which can be identified by the intensity distribution in the vicinity of the detected Bragg peak. For the 18 nm thick B-SCO film, the characteristic $(\overline{1112})$ diffraction peak from the B-SCO phase of the film aligns vertically with the STO substrate (Figure 3a), indicating the coherent strained growth without any lattice relaxation. Thus, the B-SCO films have the same in-plane lattice parameter as STO, e.g., 0.3905 nm. The out-of-plane lattice parameter of B-SCO films is calculated to be 0.393 nm. Note that B-SCO is orthorhombic ($a_0 = 5.5739$, $b_0 = 5.4697$, and $c_0 = 15.7450$ Å), which can be represented as pseudotetragonal ($a_t = 3.905$ and $c_t/4 = 3.9363$ Å). P-SCO is cubic with $a_c = 3.829$ Å. As comparatively shown in Figure 3a-c, however, we noticed that the partial annihilation of oxygen vacancies by IL and FE gating control seems to subsequently induce strain relaxation of the BTO(3.2 nm)/M-SCO(18 nm)/STO(001) sample (Figure 3b). This is most probably due to the existence of some strain gradient caused by the coexistence of B-SCO and P-SCO phases inside the buried M-SCO layer. But the M-SCO heterostructures still have the fully strained B-SCO phase in spite of the partially relaxed P-SCO phase. The *c* axis lattice constants of B-SCO and P-SCO phases in M-SCO heterostructures are 0.393 and 0.381 nm, respectively. The RSM observed for M-SCO phase is very similar to that of the M-SCO film obtained by in situ postannealing method.¹⁰ When the oxygen vacancies of the buried B-SCO layer are almost annihilated across the proximal ultrathin STO layer, the successfully converted P-SCO phase in STO(3.2 nm)/P-SCO(18 nm)/STO(001) maintains a fully strained state (Figure 3c). Also, the *c* axis lattice constant of the perovskite unit cell steeply decreased to 0.378 nm by applying -6 V gate voltages. In a word, the overall structural evolution with the intercalation of oxygen ions has been confirmed by our RSM experiments.

The structurally distinctive SCO phases will result in an obvious difference in the electronic structure. To investigate the electronic structure evolution with intercalation of oxygen ions by ILG, we used soft X-ray absorption spectroscopy (XAS) to probe elementally resolved details of the chemical valence state. Synchrotron-based XAS is a widely used technique for determining the local electronic structure with



Figure 4. (a) Schematic of the experimental setup for XAS measurements. In-plane (E//a) linearly polarized X-ray was used to measure XAS of films at cobalt L_{2,3} edge with TEY detection mode at room temperature. (b) Co L_{2,3} edge XAS curves of B-SCO (18 nm) single layer film without bias applied and with -6 V bias applied. Co L_{2,3} edge XAS curves of BTO(t)/B-SCO heterostructures under different gate voltages for t = 3.2 nm (c) and 4 nm (d). Cobalt L_{2,3} edge XAS curves of STO(t)/B-SCO heterostructures under different gate voltages for t = 3.2 nm (c) and 4 nm (d).

a detection depth of ~6 nm, 12,22,29 allowing us to detect the signals from the buried SCO layers. Figure 4a shows the schematic of the experimental setup for XAS measurements. The in-plane (E//a) linearly polarized X-ray was used to measure XAS of films at Co L_{2.3} edge in total electron yield (TEY) detection mode at room temperature. The Co $L_{2,3}$ edge XAS curves of the B-SCO (18 nm) single layer film without bias applied and with -6 V bias applied are presented in Figure 4b. The Co L_{2.3} edge XAS curves are featured as shoulder peaks on both the high- and low-energy sides of the main peaks, due to spin-orbit splitting of the cobalt 2p core hole.^{15,30} Obviously, the positions of Co L_3 edge shift toward a higher photon energy direction, e.g., from ~779.51 to ~780.28 eV, following the transition of B-SCO phase (0 V) to P-SCO phase (-6 V). This suggests an increase in cobalt valence states as the gate voltage -6 V injects oxygen ions into the B-SCO single layer film.³¹ Since a shift of ~ 0.77 eV also confirms the high oxygen stoichiometry ($\delta = \sim 0.115$) in our P-SCO phase (SrCoO_{2.885}).¹⁵

The case turns out to be dramatically different when FE BTO is grown on top of the B-SCO film. Notably, we can detect four peaks (Co $L_{2,3}$ and Ba $M_{4,5}$) in the energy range of 772–804 eV because of the partial overlap of Co L edge and Ba M edge spectra.³² Here, M_5 and M_4 in Ba M edge XAS

spectra from the ultrathin BTO layer represent the spinorbit-split $3d_{5/2}$ and $3d_{3/2}$ peaks.³³ With the application of -6V biases, the movement of the Co L₃ peak positions to higher energy is also observed in BTO(t)/B-SCO heterostructures at t = 3.2 and 4 nm, as illustrated in Figure 4c,d. However, both shifts of ~0.5 eV in Figure 4c and ~0.49 eV in Figure 4d are smaller than that of the B-SCO single layer (0.77 eV) and STO(t)/B-SCO heterostructures (~0.73 eV in Figure 4e and ~ 0.75 eV in Figure 4f). This clearly suggests that the partial transformation of the buried SCO layer gives rise to a limited increase in cobalt valence states due to the insertion of the FE BTO layer. Identically, we estimated the SrCoO_{2.75} and $SrCoO_{2.745}$ stoichiometry of buried SCO layers in BTO(t)/M-SCO and the SrCoO_{2.865} and SrCoO_{2.875} stoichiometry of buried SCO layers in STO(t)/P-SCO heterostructures. Thereby, the XAS results further confirm the oxygen-valve functionality of FE BTO in ILG experiments when negative biases are applied. Interestingly, when we applied +5.5 V biases on the BTO(4 nm)/B-SCO heterostructure, a sharp drop of the Co L_3 peak position from ~779.75 to ~778.78 eV is observed in Figure 4d. This observation implies an enhanced electric-field effect in BTO/B-SCO heterostructure when positive gate biases are applied via IL. The large photon energy shift of 0.97 eV in our case results in $\Delta \delta$ = 0.485 and



Figure 5. Magnetic and electrical transport properties of three heterostructures. (a) In-plane magnetic hysteresis loops at 10 K for B-SCO(18 nm), STO(4 nm)/P-SCO(18 nm) and BTO(4 nm)/M-SCO(18 nm) heterostructures. (b) Temperature dependent magnetization curves with field cooling, at a magnetic field strength of 1 kOe for three SCO-based heterostructures. (c) Temperature dependence of electrical resistance of three SCO-based heterostructures. (d) Strongly coupled magnetoelectric effect in multivalent strontium cobalities films under different temperature regions and resistance values. Red and light green arrows represent negative and positive gate voltages, respectively. The proton of oxygen ion is marked side of arrows. The ionic valences of Co ions and the compositions of strontium cobalities films are also involved inside the figure. PM, paramagnetism; FM, ferromagnetism; AFM, antiferromagnetism.

lower cobalt valence states, associated with the variation in oxygen stoichiometry from SrCoO_{2.5} to SrCoO_{2.015}. The roughly estimated SrCoO_{2.015} is likely related to the new $\text{SrCoO}_{2.5-\delta}^{34}$ or even $\text{HSrCoO}_{2.5}$ phases (Figure S6, Supporting Information).¹¹ It is important to note that the dissolved oxygen or water molecule inside the IL cannot be completely removed even in a high-vacuum environment, which can supply enough oxygen ions for phase transition during the gating process.³⁵ During the ILG, the water inside the IL is decomposed into negatively charged O²⁻ and positively charged H⁺ ions through electrolysis.¹¹ Thus, with positive biases, the positively charged H⁺ will accumulate at the top surface of the sample and eventually insert into the crystalline lattice to form HSrCoO_{2.5}. Also, the validity of sufficient modulation in our experiments can also be verified by a continuous shift of Co L_3 peak positions, e.g., from ~779.50 to \sim 779.95 then to \sim 780.25 eV by changing the gate bias from 0 to -4.5 and then to -6 V (Figure 4f).

Now, we address the influence of the electric field on the magnetic and electric transport properties in SCO-based heterostructures. Owing to the variations that occur in cobalt valence states and crystal structures during the phase transition, we observe a fascinating magnetoelectric coupling effect among three distinct SCO phases. Figure 5a represents in-plane magnetic hysteresis (M-H) loops of STO(4 nm)/P-SCO(18 nm), BTO(4 nm)/M-SCO(18 nm), and B-SCO(18 nm) films measured at 10 K. Corresponding magnetization—temperature (M-T) curves measured with H = 1 kOe are displayed in Figure 5b. Bulk B-SCO is an antiferromagnet with the Néel temperature (T_N) of 537 K, and the magnetic structure is the G-type in which near-neighboring Co³⁺ ions are in a high spin state but have always opposite spins.^{11,36,37} As can be seen in M-H and M-T curves, the pristine B-SCO(18

nm) sample indeed exhibits negligible magnetization, as expected from an antiferromagnet. Conversely, after subjecting the 4 nm thick BTO- and STO-capped heterostructures to -6V gate biases for 40 min, the gate-biased BTO(4 nm)/M-SCO(18 nm) and STO(4 nm)/P-SCO(18 nm) heterostructures show clear hysteresis loops, evidencing obvious ferromagnetism (FM) (Figure 5a). The difference is that the STO(4 nm)/P-SCO(18 nm) heterostructure exhibits higher saturated magnetization of about 180 emu/cm³ whereas the saturated magnetization in BTO(4 nm)/M-SCO(18 nm) heterostructure is only approximately 72 emu/cm³. Particularly, the saturated magnetization of the P-SCO phase is more than twice that of the M-SCO phase in heterostructures. In SCO system, the ferromagnetism originates from the emergence of Co⁴⁺ by oxygen intercalation, which results in an increase in the ferromagnetic exchange interaction.³⁸ The increase in Co⁴⁺ concentration, that is, the decrease in oxygen vacancy concentration, decreases the number of electrons of the down spin $\pi^*(\downarrow)$ band, which corresponds to the enhancement in magnetization.³⁹ The contrast in saturated magnetization between the M-SCO and P-SCO phase in the buried SCO layer of heterostructures also supports the oxygenvalve effect of an ultrathin FE BTO layer. Moreover, it is interesting that very similar ferromagnetic transition temperatures $(T_{\rm C})$ (~180 K) in M-SCO and P-SCO phases (Figure 5b) are also observed, ascertaining that M-SCO is indeed a physical mixture of B- and P-SCO with mixed cobalt valence states. A similar phenomenon has been reported in postannealed M-SCO¹⁰ and M-SrMnO_x⁴⁰ systems. The distribution of the two phases will be clarified below. The clear ferromagnetic signals of both M-SCO and P-SCO phases, as compared with the negligible magnetization in the B-SCO phase (antiferromagnetism (AFM)), offer the conclusive

testimony for rich variations in magnetic ground states during the electric-field-controlled phase transition.

In addition to the magnetic ground state changes, we observed a significant difference in the electrical transport properties among three distinct SCO phases. Figure 5c describes the temperature dependence of electrical resistance (R-T) curves of three SCO-based heterostructures. Apparently, the B-SCO(18 nm) sample shows a highly insulating behavior. Moreover, we observe a more than 4 orders of magnitude difference in electrical resistance between the B-SCO and P-SCO phases even at room temperature, and the STO(4 nm)/P-SCO(18 nm) heterostructure shows a metallic behavior in R-T curve. However, only near 3 orders of magnitude difference in electrical resistance between the B-SCO and M-SCO phases is observed at room temperature, and the BTO(4 nm)/M-SCO(18 nm) heterostructure still displays an insulating ground state. Specifically, a clear observation of metallic ground state in P-SCO phase indeed suggests the successful stabilization Co4+ in the STO capping case, as the insulator-to-metal transition occurs at oxygen stoichiometry δ ~ 0.1 in $\text{SrCoO}_{3-\delta}^{,9,15}$ It is also in agreement with our estimation of $\text{SrCoO}_{2,875}$ in buried P-SCO layer by XAS shifting. For the BTO capping case, the insulating ground state of M-SCO phase implies the δ value is greater than the value of P-SCO phase ($\delta = 0.125$) but is still less than 0.5 in B-SCO phase. Hence the estimated off-stoichiometric M-SCO phase of SrCoO_{2.745} by XAS is also reasonable. A chemically inertia capping layer profoundly affects oxygen vacancy formation/ annihilation and migration in ILG, leading to the formation of rich magnetoelectric phases in the buried SCO layer, as shown in the magnetoelectric phase diagram of Figure 5d. Thus, if we selectively control the phase transition with an electric field and an appropriate capping layer, the corresponding magnetic and electronic states will be controlled simultaneously, and hence the potential multistate magnetoelectric memories can be obtained.

Since we have achieved the remote control of oxygen vacancies and phase transition as well as acquired three distinct phases in SCO-based heterostructures by ILG, an explanatory mechanism is needed to provide a physical understanding of IL modulating process. We should emphasize that the primary driving force for inducing phase transition in SCO-based heterostructures is the induced electric-field-driven electrochemistry (oxygen migration) rather than electrostatic doping, because the nonvolatile electric-field effect could not be generated by electrostatic doping. For the single SCO layer case, the modulation mechanism is schematically illustrated in Figure 6a. SCO ($SrCoO_r$) is employed here because its oxygen component could be manipulated by IL, accompanied by the phase transition between different distinct phases. When the gate voltages are applied, cations and anions in IL are electrostatically attached to the external gate electrodes and IL/SCO interface. Subsequently, EDLs which are pairs of sheets of negative and positive charges consisting of the ions in the IL and the induced charges on the surface of SCO, are formed. Since the distance of paired charges inside the EDL is on the order of the size of anions and cations (~1 nm), 5,41 the electric field generated by EDL at the interface between IL and SCO layer is very high (on the order of 10 MV/cm).¹² In this case, the negative gate bias injects the oxygen ions into the SCO film and accompanied by the extraction of electrons from SCO film.³⁹ Thus the negative gate bias drives the phase transition from B-SCO to P-SCO phases (Figure 6a).

Single films (a) **B-SCO** P-SCO STO substrate BTO capping STO capping (c) (b) EDI -like-1 STO EDL BTO EDL-like-2 SCO STO substrate STO substrate DEME⁺ cation TFSI⁻ anion Hole Electron • O²⁻ (oxygen ion) O oxygen vacancy Electric dipole

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Figure 6. Schematic the mechanism of electric-field modulation by ILG for (a) SCO, (b) BTO/SCO, and (c) STO/SCO. The direction of BTO polarization and the recycle of electron exchange and oxygenion migration are labeled by pink and red arrows, respectively. When negative gate voltages ($V_{\rm G} < 0$) are applied on the IL and thin film, negatively charged TFSI⁻ ions in IL move to the interface between the IL and thin film, which causes the accumulation of holes (small black spheres) on the side of the thin film and results in an electric double layer (EDL) at the interface. The driving potential of the EDL can insert the O^{2-} ions (small red spheres) into the film accompanied by the extraction of electrons from SCO films, as indicated by the red arrows. The oxygen vacancies (small yellow hollow circles) in films may supply a preferential oxygen transport lane for oxygen migration.

For the BTO capping case, with the application of gate voltages, the two EDLs (EDL-like-1 and EDL-like-2) are formed and superimposed together due to the existence of an electric dipole inside the BTO layer (Figure 6b), which caused an enhancement of the electric field at the interface between SCO and BTO.²² Unlike manganites, we cannot describe the systems as local t_{2g} moments plus itinerant e_g electrons. In SrCoO₃, the intersite exchange interaction is mediated by both the majority e_g and the minority t_{2g} electrons. The minority e_g electrons participate in Co-O bonding but are not active in the double exchange.⁴² This implies that the t_{2g} electrons are important for dominating the magnetoelectric properties of SCO. Previously, we have demonstrated the preferential inplane orbital occupancy for the tensile SCO film on STO substrates associated with coupled intermediate spin-Co⁴⁺ $(t_{2g}^4 e_g^{\ 1})$ /high spin-Co³⁺ $(t_{2g}^4 e_g^{\ 2})$ states.¹⁵ This means that there are always unoccupied t_{2g} orbital states in SCO. These unoccupied out-of-plane $d_{xz/yz}$ orbitals would mainly contribute to form Ti-O-Co hybridization bond at BTO/SCO interface. For the negative gate voltage case, the electric dipole points away from the bottom SCO (Figure 6b); hence, there are negative bound charges at the SCO/BTO interfaces. This will repel electrons in out-of-plane $d_{xz/yz}$ states of t_{2g} orbitals of cobalt ions and raise the energy of out-of-plane $d_{xz/yz}$ states. This process has been theoretically detected in the Sr₂CoMoO₆/BTO interface.⁴³ As a result, the different interface bound charges between positive/negative gate biases will change the orbital occupations, which subsequently influences the hybridization of Ti-O-Co hybridization bond. The interfacial Ti-O-Co bond here is the important vertical channel for electron injection and extraction in SCO/ BTO and SCO/STO through the tunneling effect.^{22,24} The negative gate voltage drives the Ti ions away from the Co ions

and extends the distance between Ti and Co, reducing the charge overlap and weakening the concomitant Ti-O-Co bond. The electron exchanges and oxygen migration under negative gate voltages are accordingly weakened. In this case, there is a strong competing interaction between the vertical electron tunneling and FE polarization, which finally results in the formation of an oxygen valve and the surprising emergence of M-SCO phase as the BTO thickness varies from 3.2 to 4 nm. When the thickness of BTO is very thin (1.6-2.4 nm), the FE polarization is absent/or very weak, and the electrons can almost tunnel from SCO to IL so that oxygen ions can be injected into the SCO layer across the BTO layer. If the BTO is quite thick (8-20 nm), the attenuation of the electron tunneling effect, which is coupled with the enhancement of FE polarization, results in no electric-field modulation effect. It is noted that although our explanation mechanism based on the concept of an interfacial hybridization bond is similar to the BTO/(La,Sr)MnO₃ case by ILG,²² the modulation is totally different from that case where an orbital switch is formed on the $BTO/(La,Sr)MnO_3$ interface. When the negative gate voltages are applied, the orbital switch is in "OFF" state and there is no electric-field modulation effect. However, we can successfully obtain remote modulation here by ILG and the oxygen valve is formed in BTO/SCO heterostructures when negative gate voltages are applied. In addition to the "orbital switch" effect caused by e_g orbitals alone just like in manganites, the response of t_{2g} orbitals to the electric-field effect in cobaltite is first disclosed by the unique oxygen valve effect. Therefore, the two situations in BTO/SCO and BTO/ (La,Sr)MnO₃ interfaces are not contradictory but complementary to each other.

To acquire more experimental evidences to clearly show the important role of FE polarization in the smaller gating effect of the oxygen valve, we also changed the BTO to $PbTiO_3$ (PTO) layer to perform the same ILG experiments because of the well-known stronger FE polarization of PTO than that of the BTO layer (Figure S7, Supporting Information). Interestingly, we found that the stronger FE polarization causes a smaller gating effect. This well proves the important role of FE polarization in controlling the gating effect and oxygen valve formation.

The present discussions reasonably explain the important role of the competition between electron tunneling and FE polarization in a smaller gating effect in the case of BTO/SCO. However, how oxygen ions can migrate through the BTO layer to reach the SCO layer still needs to be identified since both BTO and STO are not good ionic conductors, especially at room temperature. We can first exclude the memristors' behavior just like in Pt(Ag)/BTO or STO/Pt structure,^{44,45} because the gate electrode of aluminum foil is very far from the sample surface (~4 mm) in our ILG experiments (see Methods). In memristors, the Pt/Ag electrode is directly in contact with the BTO or STO surface with a concentrated electric field, easily causing a soft breakdown in ultrathin ferroelectric/dielectric gate oxide layers.46 No noticeable damage at the surface of gated BTO/B-SCO sample was observed (Figure S8, Supporting Information), indicating the reliability of our ILG experiments. We believe that -6 V gate biases mainly drive oxygen migration into the SCO through the BTO layer and induce the phase transformation.

To examine the oxygen channeling effect inside the BTO layer, the depth-dependent electron energy loss spectroscopy (EELS) was further carried out in BTO(4 nm)/B-SCO samples before and after IL gating (Figure S9, Supporting Information). It is found that there is a slight shift in Ti $L_{2,3}$ edge from BTO surface to the BTO/SCO interface in a pristine BTO layer (Figure S9a-c, Supporting Information), suggesting that there are as-grown intrinsic oxygen vacancies in the BTO layer. Interestingly, the obvious shift in Ti $L_{2,3}$ edge from BTO surface to the BTO/SCO interface in the gated BTO layer (Figure S9d-f, Supporting Information) was observed and the buried SCO layer successfully changed to the M-SCO phase. This indicates that the concentration of oxygen vacancies is increased from BTO surface to the BTO/ SCO interface due to the application of negative gate voltages. These oxygen vacancies may supply a preferential oxygen transport lane for oxygen migration, that is, the oxygen ions can penetrate the 4 nm BTO layer into SCO. This is fully consistent with the result reported by Sharma et al. that oxygen can penetrate the 3-4 nm FE-PbZr_{0.2}Ti_{0.8}O₃ layer by ILG.⁴⁷ These findings demonstrate that the large electric field induced by IL biasing drives oxygen migration across the BTO layer into the SCO assisted by oxygen vacancies inside the BTO layer and induces SCO phase transformation. Therefore, we concluded that the coexistence of ferroelectricity and surface electrochemical changes (oxygen-ion migration) inside the ultrathin BTO layer acts as the oxygen valve.

The situation becomes different for the STO capping where the insert of the STO layer just reduces the initial electric field due to the increase of EDL thickness, as shown in Figure 6c. Although the existence of the 4 nm thick STO (1.6-4 nm)would weaken the electric field inevitably, the electric-field effect generated here is still much larger than that when simply using the traditional ~ 100 nm thick dielectric.⁴⁸ Since there is no tunnel barrier from FE polarization, almost all electrons can still tunnel from the SCO film into the IL across the STO layer under a relatively large electric field. Thus, the oxygen ions can migrate into the SCO film across the STO layer associated with the sufficient phase transition of the buried SCO layer. However, the phase transition from B-SCO to P-SCO under 8 nm thick STO capping layers still can be finished. This may be attributed to the stronger oxygen diffusion ability of the STO layer⁴⁹ plus some inevitable defects, e.g., oxygen vacancies inside the STO layer. These defects can form a localized state and subsequently assist the inelastic electron tunneling in forming a thicker barrier.⁵⁰ When the thickness of STO is up to 20 nm, the electron tunneling and oxygen-ion migration are totally blocked. In brief, these results cannot be explained by an electrostatic gating effect but by the oxygen migration effect with long-range interaction.

Considering that the XRD peak positions of both phases in M-SCO-based heterostructures are identical to those from individual B-SCO and P-SCO films (Figure 2), it can seemingly be speculated that the stable M-SCO phase is due to the coexistence of B-SCO and P-SCO phases. The above XAS and magnetoelectric properties also confirm the mixed feature of M-SCO phase. Interestingly, a very similar phenomenon has been observed in postannealing M-SCO¹⁰ and M-SrFeO_x⁵¹ single-layer films. However, how the two phases are physically arranged within these M-SCO and M-SrFeO_x layers is not clear so far. Are the two phases evenly distributed or are they arranged vertically up and down or horizontally left and right? So we still need to further clarify the positions of different phases inside the M-SCO layer.

For direct visualization of the crystalline structure of M-SCO phase in our case, STEM was performed on BTO(4 nm)/B-



Figure 7. Structural information of the M-SCO phase and related EELS characterization. (a) HAADF-STEM image of pristine BTO(4 nm)/B-SCO heterostructure. (b) HAADF-STEM image of -6 V gated BTO(4 nm)/B-SCO heterostructure. Enlarged HAADF- (c) annular bright field (ABF) and ABF-STEM (d) images from the dashed red rectangular box of (b) showing the P-SCO phase. Enlarged HAADF- (e) and ABF-STEM (f) images from the dashed cyan rectangular box of (b) showing the B-SCO phase. EELS spectra of O K edge (g) and Co L_{2,3} edge (h) of B-SCO phase (blue line) and P-SCO phase (red line) in the M-SCO layer of heterostructure.

SCO samples in the pristine state (before gating) and ex situ gated state. Figure 7a shows the HAADF-STEM image of pristine BTO(4 nm)/B-SCO heterostructure along the STO[110] direction. Here, the alternate stacking of fully oxygenated octahedral and oxygen-deficient tetrahedral sublayers in a buried SCO layer is observed directly and is consistent with the brownmillerite structure in Figure 1c along the STO[100] direction. Figure 7b represents the typical HAADF-STEM image of M-SCO phase in gated BTO (4 nm)/SCO sample. Dramatically, the M-SCO phase is laterally composed of P-SCO phase dominating in the left part and B-SCO phase dominating in the right part, marked by the white dashed line representing the phase boundary. Previously, Wang et al.⁴⁰ reported the postannealed M-SrMnO_x film consisting of the vertically aligned P-SrMnO_{3- δ} phase and B-SrMnO_{2.5} phase at the top and bottom parts, respectively. We emphasized that even under high temperature and high oxygen pressure condition in PLD chamber, only the top portion of SrMnO_{2.5} can undergo a structural phase transition into the P-SrMnO_{3-δ} phase, leaving unconverted B-SrMnO_{2.5} phase at the bottom part. So the lateral coexistence of B-SCO and P-SCO phases here further demonstrates our sufficient modulation across the BTO layer by electric-field-controlled ILG. In addition, the transversely arranged P-SCO and B-SCO

phases are also consistent with the ILG results in SCO single layers recently reported by Cui et al.⁵² via using in situ and real-time high-resolution transmission electron microscopy. They pointed out that the phase transformation boundary in the SCO layer moves at a velocity that is highly anisotropic, traveling at speeds ~30 times faster laterally than through the thickness of the film.

To analyze the detailed oxygen vacancy distribution and electronic structure difference between the two phases, the enlarged STEM images are further extracted from the dashed red and cyan rectangular boxes, respectively, representing the P-SCO phase and B-SCO phase. The HAADF images suggest that the P-SCO phase has a uniform perovskite structure with the stacking of octahedral CoO₆ layers (Figure 7c), whereas B-SCO phase possesses alternating stacks of CoO₄ tetrahedral and CoO₆ octahedral sublayers, accompanied by spatial distance modulation of Co-Co atomic pairs within the oxygen-deficient CoO₄ tetrahedral sublayers (Figure 7e). Such collective displacements of Co ions in the CoO₄ tetrahedral layers of B-SCO phase create well-ordered oxygen vacancy superstructures. Thus, alternating CoO₂ and CoO sublayers are observed in the ABF image of the B-SCO phase (Figure 7f), in contrast to the fully oxygenated CoO_2 layers, as revealed by the ABF image of P-SCO phase (Figure 7d). The electron energy loss spectroscopy (EELS) spectra at O K edge and Co $L_{2,3}$ edge further reveal the electronic structure difference in the two phases. The EELS spectra were normalized. The stronger pre-edge peak intensity of the P-SCO phase than that of the B-SCO phase in O K edge EELS spectra was observed due to the stronger O 2p–Co 3d hybridization at the higher cobalt oxidation state,^{9,11,15} as shown in the shadow area of Figure 7g. Meanwhile, compared with the B-SCO phase, the integrated white line L_3/L_2 intensity ratio of Co $L_{2,3}$ edge in the P-SCO phase is smaller ($L_3/L_2 = 3.09$ for P-SCO, and 3.26 for B-SCO) in Co $L_{2,3}$ edge EELS spectra (Figure 7h),^{34,52,53} in agreement with the expected Co³⁺ and Co⁴⁺ ion concentrations in the B-SCO phase and P-SCO phase, respectively.

CONCLUSIONS

In conclusion, the voltage-driven oxygen vacancy formation/ annihilation and migration in buried B-SCO films hybridized with insulating BTO and STO layers has been demonstrated through ILG, allowing for the controlled occurrence of a topotactic phase transition and generation of the rich magnetoelectric coupling effect. Compared with ultrathin dielectric STO capping, the strong competing interaction between FE polarization and vertical electron tunneling produces an additional energy barrier for oxygen ions transporting across the BTO/SCO heterointerface, which causes a surprising emergence of M-SCO phase in ultrathin BTO-capped heterostructures. The surface electrochemical changes (oxygen-ion migration) in BTO itself also play some role in oxygen migration. Moreover, the lateral coexistence of the P-SCO phase and B-SCO phase, respectively, dominating in left and right parts in the M-SCO phase is directly observed by STEM. Our results clearly suggest that inserting a proper FE polarization layer in the oxide-electrolyte interface provides a gentle way to control oxygen flow across the interface, thus building a new concept of the oxygen valve. Meanwhile, the realization of an electric-field-controlled tristate phase transition in SCO films based on appropriate capping layers will also further stimulate the development of low-power-cost multistate memories and sensors.

METHODS

Sample Preparation. The single brownmillerite $SrCoO_{2.5}$ (B-SCO) films, STO/B-SCO, and BTO/B-SCO heterostructures were grown on the (001)-oriented SrTiO₃ (STO) substrates by pulsed laser deposition (PLD) system with a 248 nm wavelength KrF excimer laser from the stoichiometric $SrCoO_3$, $BaTiO_3$, and $SrTiO_3$ targets. The growth temperature/oxygen background pressures for SCO, BTO, and STO were 720 °C/200 mTorr, 720 °C/4 mTorr, and 720 °C/20 mTorr, respectively. The growth was monitored in situ by reflection high-energy electron diffraction (RHEED) analysis, allowing precise control of the thickness at the unit cell scale and accurate characterization of the growth dynamics. After growth, the single B-SCO films were cooled down to room temperature at a cooling rate of 8 °C/min in 2 Torr oxygen pressure and the STO/B-SCO and BTO/B-SCO heterostructures were cooled down to room temperature in 500 Torr of oxygen pressure at a rate of ~S °C/min.

Ionic Liquid Gating (ILG) Experiments. The ionic liquid (IL) N,N-diethyl-N-(2-methoxyethyl)-N-methylammonium bis-(trifluoromethylsulfonyl)imide (DEME-TFSI) was used as an electrolyte to apply gate voltages. Usually a 2.5 mm \times 5 mm sample was adhered to the chip carrier for the application of gate voltages. Before the ILG, a layer of aluminum foil was set up above the sample, and two long edges of the sample were wrapped in a "boat" shape and painted with double-sided tapes, thus leaving about a 4 mm space

between the aluminum foil and the sample surface. Meanwhile, the aluminum foil is also adhered to the partial electrodes of chip carrier with silver conductive paste as the gate electrode. One short edge of the thin films was bonded to the partial electrodes of the chip carrier with the ultrasonic spot welding machine as the bottom electrode. A small syringe was used to inject a certain amount of IL in the space between the aluminum foil and the sample. Finally, the device was put into a homemade electrical measurement box for the application of gate biases. Electrical biases were applied between the thin film and gate electrode, using a cell configuration as shown in Figure S10 (see the Supporting Information). All samples are applied with different gate voltages for 40 min for sufficient modulation. After gating, the IL was removed by washing the sample with acetone and then alcohol for the ex situ measurements.

Structure Characterization. The crystal structure of all films was characterized by X-ray diffraction (XRD; Rigaku SmartLab X-ray Diffractometer, Cu K α radiation) at Tsinghua University. The X-ray reciprocal space mappings of the films were measured by using a Bruker X-ray diffractometer equipped with thin-film accessories (D8 Discover, Cu K α radiation) at the Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences. The atomic resolution aberration-corrected high-angle annular dark field (HAADF) and annular bright field (ABF) scanning transmission electron microscopy (STEM) images as well as electron energy loss spectroscopy (EELS) spectra were taken by the FEI Titan Cubed Themis G2 60–300 on samples prepared using a dual-beam focused ion beam system.

Magnetoelectrical Property Measurements. A superconducting quantum interference device magnetometer was used to measure the magnetic properties of SCO-based heterostructures, including the magnetic hysteresis (M-H) loops and temperature-dependent magnetization (M-T) curves, with the magnetic field applied along the in-plane direction of the films. In-plane electrical transport measurements were conducted using the ex situ gated film devices with a four-probe method in a 9 T mini Cryogen-Free Measurement System for Precision Measurement of Physical Properties (CFMS-9, Cryogenic Limited, U.K.) in a cooling process. The ferroelectricity of BTO films was probed by the piezoresponse force microscope (PFM).

Synchrotron X-ray Absorption Spectra. X-ray Cobalt $L_{2,3}$ edge XAS measurements were performed in total electron yield (TEY) detection mode at room temperature at Beamline BL08U1A of Shanghai Synchrotron Radiation Facility (SSRF). Before measuring cobalt $L_{2,3}$ edge XAS, we first need to wait for 1–2 h for the stabilization of beamline energy. Then, we check it with a standard sample to confirm no shifting in beamline energy. All spectra were collected at a normal incidence of radiation with respect to the film surface. The energy resolution of the absorption spectra was set to 0.3 eV. The cobalt $L_{2,3}$ edge XAS spectra were normalized to the maximum intensities of Co L_3 peak.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b02442.

Additional details and figures on the film growth, ferroelectricity of ultrathin BTO films, original XRD data of BTO(t)/B-SCO and STO(t)/B-SCO heterostructures, the steady state evaluated by time dependence of the gate current ($I_{\rm G}$) in ILG, the control experiments for ILG-induced phase transition, emergence of HSrCoO_{2.5} phase for ILG-induced phase transition, ILG experiments performed on PTO/SCO heterostructures, atomic force microscopy images before and after ILG, the depth-dependent EELS, and the schematic ILG of cobaltite-based heterostructures at room temperature (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: songcheng@mail.tsinghua.edu.cn (C.S.). *E-mail: wliu@imr.ac.cn (W.L.).

ORCID 💿

Cheng Song: 0000-0002-7651-9031 Jirong Sun: 0000-0003-1238-8770 Jing Zhu: 0000-0002-2175-9476

Author Contributions

^VY.G. and K.X. contributed equally to this work.

Author Contributions

C.S. and W.L. conceived and designed the experiment and the study. Y.G. prepared the samples, carried out XRD, XAS, measurement of magnetization and electrical transport properties, and processed the experimental data. K.X., X.Z., and J.Z. performed the STEM and EELS characterization and analysis. H.Z. and J.S. carried out the RSM measurements. H.M. and M.S.S. provided advice on the BTO film growth, PFM characterization, and ILG experiment. Z.Z. and F.P. oversaw the projects. Y.G., W.L., and C.S. interpreted the data and wrote the manuscript. All of the authors contributed to the discussion of the results and commented on the manuscript.

Notes

The authors declare no competing financial interest.

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