Direct imaging of structural changes induced by ionic liquid gating leading to engineered three-dimensional meso-structures

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The controlled transformation of materials, both their structure and their physical properties, is key to many devices. Ionic liquid gating can induce the transformation of thin-film materials over long distances from the gated surface. Thus, the mechanism underlying this process is of considerable interest. Here we directly image, using in situ, real-time, high-resolution transmission electron microscopy, the reversible transformation between the oxygen vacancy ordered phase brownmillerite SrCoO$_{2.5}$ and the oxygen ordered phase perovskite SrCoO$_3$. We show that the phase transformation boundary moves at a velocity that is highly anisotropic, traveling at speeds ~30 times faster laterally than through the thickness of the film. Taking advantage of this anisotropy, we show that three-dimensional metallic structures such as cylinders and rings can be realized. Our results provide a roadmap to the construction of complex meso-structures from their exterior surfaces.
The use of electrical methods to manipulate the ground states of correlated-electron oxides has much potential for the development of electronic and iontronic devices\textsuperscript{1–11}. One method is to take advantage of the very high electric fields that are generated by polarizing ionic liquids (IL). This method has enabled, for example, the reversible transformation of thin oxide films between insulating and metallic\textsuperscript{1,4,8–10,12} or superconducting states\textsuperscript{8}. In some cases it has been shown that these IL gate-induced transformations are predominantly the result of electric-field-induced structural changes that rely on the migration of oxygen\textsuperscript{4,10}. However, the detailed mechanisms underlying these processes are poorly understood. Thus, the visualization of oxygen migration under IL gating by direct observation at the atomic level is of great interest. In situ high-resolution transmission electron microscopy (TEM) is an excellent technique for such studies, but a major challenge is that the IL strongly degrades the image quality due to scattering of the electron beam\textsuperscript{13}. We overcome this obstacle by positioning a droplet of the IL close to, but not within, the imaged region of the TEM lamellae by the use of an atomic force microscope.

For these studies, we chose to explore two phases within the strontium cobaltite family (SrCoO\textsubscript{3}, SCO), namely the perovskite (P) phase SrCoO\textsubscript{3} and the brownmillerite (BM) phase SrCoO\textsubscript{2.5}. These phases have been extensively studied: SrCoO\textsubscript{2.5} is an antiferromagnetic insulator, whereas SrCoO\textsubscript{3} is a ferromagnetic metal\textsuperscript{14}. Here, we find direct evidence for massive oxygen migration induced by liquid gating of SrCoO\textsubscript{3} thin films. We find that the migration takes place over several minutes and that its time-scale is an order of magnitude faster parallel, as compared to perpendicular to the time-scale is an order of magnitude faster parallel, as compared to perpendicular to the surface. Taking advantage of these findings we create a series of three-dimensional meso-structures in SrCoO\textsubscript{x} and several other oxide films.

Results

Experimental setup for in situ TEM IL gating. In these studies, SrCoO\textsubscript{2.5} films, 40 nm thick, were prepared by pulsed laser deposition (PLD) on (001) SrTiO\textsubscript{3} (STO) and 0.5 wt% Nb-doped SrTiO\textsubscript{3} (NSTO) substrates. A single STO wafer was used to prepare samples for: in situ TEM and STEM (scanning transmission electron microscopy), ex situ STEM (samples ST-A and -B), and transport measurements, while samples on NSTO were used for meso-structure fabrication and conductive atomic force microscope (CAFM) measurements. Lamellae for the TEM studies were prepared using standard thinning techniques and supported on an in situ chip holder with electrodes for the application of a gate voltage ($V_G$). As schematically shown in Fig. 1, a droplet of the IL was positioned to cover both the sample and a lateral gate electrode that formed part of a field effect transistor (FET) (see Fig. 1a and more details in Methods and Supplementary Fig. 1 and 2). The channel of the FET is formed from a thin film of SrCoO\textsubscript{2.5}. While applying a voltage to the gate electrode, reversible changes between the BM SrCoO\textsubscript{2.5} and the perovskite SrCoO\textsubscript{3} phases could be contemporaneously observed in the lamellae (Fig. 1b). Indeed, consistent with our TEM observations, the film is converted from an initially insulating state to a final metallic state (see Fig. 1c).

**In situ observation of structural changes induced by gating.** The structure of the BM SrCoO\textsubscript{2.5} is an oxygen vacancy ordered phase that is derived from the perovskite phase SrCoO\textsubscript{3} by removal of one oxygen atom in every other CoO\textsubscript{2} sublayer. The crystal lattice of the pristine SrCoO\textsubscript{2.5} sample, as shown in the high-resolution TEM image in Fig. 2a, is characterized by a modulated structure (unit-cell doubling along the $c$-direction). This modulation is also seen in corresponding superlattice reflections in the FFT (fast Fourier transform) diffractograms of the TEM lattice plane images, as indicated by small yellow circles in Fig. 2b. After the application of $V_G = -3$ V for 5 min, the modulated structure in the area near the surface of the thin film changes to the perovskite structure, consistent with the weaker superlattice reflections in the FFT diffractograms (Fig. 2c, d). This is consistent with injection of oxygen into the material, resulting
in the transition: SrCoO$_{2.5}$ $\rightarrow$ SrCoO$_3$. The yellow dashed lines in the TEM images in Fig. 2 mark the approximate boundary between the BM and the perovskite SCO phases. With increased gating time (8 and 10 min in Fig. 2e–h, respectively), the SrCoO$_{2.5}$ $\rightarrow$ SrCoO$_3$ transition evolves from the surface to the bottom of the thin film. This phase transition is completed after $\sim$12 min (Fig. 2i, j). Energy dispersive x-ray spectroscopy confirms a significant increase in oxygen content as a result of the gating process that is also clearly non-volatile (see Supplementary Figs. 3 and 4).

Subsequently, we applied a reversed polarity gate voltage $V_G = +2.5$ V. As shown in Fig. 2k–p, when the gating time is increased, the modulated structure first appears at the surface and then gradually extends to the bottom of the film, accompanied by enhanced superlattice reflections. This is direct evidence that $V_G = +2.5$ V creates oxygen vacancies ($V_O$) in the sample.
resulting in the phase transition SrCoO$_3$ → SrCoO$_{2.5}$. Such a reversible, non-volatile, electrical manipulation between the two SCO phases, unambiguously demonstrates the role of $V_O$ in the IL gating process. This phase transition is also confirmed by X-ray diffraction (XRD) from large area thin-film samples and $V_G$ dependent resistance curves measured in FET devices (see Supplementary Figs. 5 and 6).\textsuperscript{15} We note that the IL gate-controlled phase transition is reproducible, and any electron beam irradiation effects can be ruled out (see Supplementary Figs. 7 and 8). The reversible phase transition that extends from the surface to the bottom of the film can be followed more closely by depth-dependent line-scan FFT diffractograms (see Supplementary Fig. 9). From Fig. 2c–i, the phase boundary moves ~20.3 nm over a 7 min period when $V_G = -3$ V, while from Fig. 2k–o, the phase boundary moves ~18.0 nm over 5 min when $V_G = +2.5$ V. The speed of the vertical phase transition is thus estimated to be $\approx 2.9$ nm min$^{-1}$ for SrCoO$_{2.5}$ → SrCoO$_3$, and $\approx 3.6$ nm min$^{-1}$ for SrCoO$_3$ → SrCoO$_{2.5}$.

In addition to the vertical oxygen transport across the thin film, lateral oxygen transport within the thin film also takes place. This can be seen by inspecting TEM images of the film at different lateral distances $d$ from the IL droplet, as shown in Fig. 3a. Images taken at $d = 1.03$, 1.19, and 1.51 $\mu$m are shown in Fig. 3b–d, respectively, after $V_G = -3$ V was applied for 12 min. The area in Fig. 3b is very close to that shown in Fig. 2, where the sample has been fully converted to SrCoO$_3$. As $d$ is increased to $\approx 1.19$ $\mu$m, both SCO phases are found and the phase boundary is marked by a yellow dashed line in Fig. 3c. Remarkably, the SrCoO$_3$ phase occupies a much larger area closer to the IL and near the film surface, indicating that oxygen ions migrate first from the IL towards the other end of the thin film through the surface. In contrast, at $d = 1.51$ $\mu$m (Fig. 3d), the structure appears to be unaffected by $V_G$. As distinct from the vertical oxygen transport, the lateral oxygen transport displays a much higher velocity of $\approx 10^2$ nm min$^{-1}$. This high speed oxygen transport could be attributed to a surface “fast oxygen” transport lane, where the decreased number of bonds and reconstruction phenomena will considerably reduce the activation energy for atom jump processes.\textsuperscript{16} Note that the lateral migration rate of O$_2^-$ that we observe at room temperature in SCO is comparable to that of some cathode materials in solid oxide fuel cell (SOFC) but which occurs at very high temperatures of $\sim 700$ °C.\textsuperscript{17,18}

![Fig. 3](image-url) Distance-dependent ionic liquid gating effect. a Overview of in situ TEM sample, where the selected areas for high magnification images are marked by red boxes. The white scale bar in a corresponds to 200 nm. The edge of the ionic liquid (IL) is indicated by a blue dashed line. The distances between the ionic liquid and selected areas are estimated with respect to the red point and the centers of the red frames. The TEM images of selected areas at different distances from the edge of the IL, after gating at $V_G = -3$ V for 12 min: b $d = 1.03$ $\mu$m; c $d = 1.19$ $\mu$m; and d $d = 1.51$ $\mu$m. The interface between the SCO film and the STO substrate is shown as a white dashed line. The yellow dashed line in c shows the boundary between brownmillerite (BM) and perovskite (P) SCO phases. The white scale bars in b–d are 5 nm.

**Oxygen vacancy distribution and electronic structure.** STEM-HAADF (high angle annular dark field) and STEM-ABF (annular bright-field) measurements were used to further probe the distribution of oxygen ions or vacancies. Due to the non-volatility of the IL gating effects,\textsuperscript{4,8–10} ex situ gated samples were used to obtain higher resolution images. Two cross-sectioned samples were prepared for these studies: sample ST-A was first gated at $V_G = -3$ V followed by a second gating at $V_G = +2.5$ V, while sample ST-B was gated at $V_G = -3$ V. The gating time for each $V_G$ was 30 min. For these ex situ experiments, the samples were $[110]$ oriented in-plane so as to better observe the ordering of the VO channels along $[110]$ (for the in situ experiments discussed above the sample was $[100]$ oriented in-plane). The HAADF images show that the structure of ST-A consists of alternate stacking of fully oxygenated octahedral (SrO–CoO$_2$–SrO) and oxygen-deficient tetrahedral (SrO–CoO–SrO) sublayers, whereas ST-B has a uniform perovskite structure (compare Fig. 4a, b). Another clear distinction between the two samples is the pairing of the Co atoms within the tetrahedral sublayers in sample ST-A resulting from the ordering of the oxygen vacancies that can be clearly seen in Fig. 4a.

The ABF images taken concurrently with the HAADF images, exhibit an opposite contrast and are more sensitive to light elements.\textsuperscript{19} In Fig. 4c, d, Sr, Co, O, and $V_O$ sites in the ABF images are indicated by yellow, red, and orange spheres, and orange circles, respectively. By comparing the ABF images for samples ST-A and -B, one can clearly see the columns of $V_O$, which are located between the Co–Co pairs (orange circles in
magnetization studies on thin-

at the higher Co oxidation state20. Meanwhile, compared with ST-A, the Co energy with a smaller for sample ST-B (Fig. 4g), where the Co and O sites are valleys (Fig. 4e, g) while 

property changes caused by IL gating are also con 

indicating the ferromagnetic character of ST-B. The magnetic 

VO24 and WO39, ~5% in SmNiO35 and (La,Sr)MnO38. Moreover, 

found in earlier studies of the IL gating of other oxides: ~3% in 

massive oxygen addition and removal is much higher than those 

- Fig. 4 Crystal and electronic structure of ex situ gated samples. STEM-HAADF images of a Sample ST-A and b Sample ST-B. STEM-ABF images of c Sample ST-A and d Sample ST-B, respectively. The higher the atomic number, the brighter (darker) the atom in HAADF (ABF). The white scale bars in a-d are 1 nm. Sr, Co, O, and V0 sites are indicated by yellow, red, and orange spheres, and orange circles, respectively. Intensity line-scans of the ABF images of e Co2O and f CoO sublayers in Sample ST-A, and g Co2O sublayer in Sample ST-B. The line-scans correspond to the green, blue and red boxes as indicated in the ABF images, respectively. h O-K EELS; i Co-L EELS; and j Co-EMCD of Sample ST-A and ST-B. The pre-peak in the O K-edge is highlighted in yellow.

Beyond changes in crystal structure, the electronic structure and magnetic properties are also dramatically affected by IL gating. In electron energy-loss spectroscopy (EELS) at the O K-edge (Fig. 4h), the pre-peak intensity of sample ST-B is higher than that of ST-A due to the stronger Co 3d–O 2p hybridization at the higher Co oxidation state20. Meanwhile, compared with ST-A, the Co L-edge of ST-B in Fig. 4i shifts to a ~1.0 eV higher energy with a smaller L3/L2 intensity ratio (L3/L2 = 2.84 for ST-A, and 1.96 for ST-B), consistent with that for expected for Co3+ and Co4+ (ref. 21). Such a change in electronic structure is confirmed by X-ray absorption spectroscopy (XAS) (see Supplementary Fig. 10). These crystal and electronic structure changes show convincingly that ~0.5 oxygen per formula unit (~17%) is added or removed during the IL gating process in ST-A (SrCoO2.5) and ST-B (SrCoO3), respectively. Note that such a massive oxygen addition and removal is much higher than those found in earlier studies of the IL gating of other oxides: ~3% in VO24 and WO39, ~5% in SmNiO35 and (La,Sr)MnO38. Moreover, an electron energy-loss magnetic chiral dichroism (EMCD) signal at the Co L-edge is clearly seen in sample ST-B (see Fig. 4g and Supplementary Fig. 11) but not in sample ST-A22,23, clearly indicating the ferromagnetic character of ST-B. The magnetic property changes caused by IL gating are also confirmed by magnetization studies on thin-film samples (see Supplementary Fig. 12), which are consistent with ferromagnetic and antiferromagnetic ground states in SrCoO2.5 and SrCoO3, respectively, as found in the bulk14.

**IL gate engineered meso-structures.** The multi-directional oxygen transport, that was directly observed above, allows for the possibility of creating complex meso-structures by local IL gating. To demonstrate this possibility, we have created patterns of orifices in resist layers that were spin-coated onto several distinct oxide films that show different degrees of anisotropic oxygen ion transport. Here we present data on IL gated (001) oriented VO2, La0.45Sr0.55MnO3, and SrCoO2.5 films that were each covered by resist layers, patterned using electron beam lithography to have orifices 1 μm in diameter, spaced 2 μm apart (see Supplementary Figs. 13 and 14). The resist is covered by the IL but the oxide films only “see” IL within the orifices. Thus, on gating, an electric double layer can only be formed within these limited regions at the oxide surface. All the samples could be changed from a high-resistance state to a low-resistance state by gating (see Supplementary Fig. 15)4,10,24. After gating, the IL and resist are removed and CAFM imaging is carried out to profile the conductivity of the films within and without the orifices.

Typical CAFM results are shown in Fig. 5a–c. The films of (001) VO2 display a metal–insulator transition above room temperature (see Supplementary Fig. 15) so the films are poorly conducting at ambient temperature. After IL gating we find clear evidence that only within the orifice is there a change in the film...
conductivity, with a substantial increase in conductivity: the regions covered by resist are not affected at all by the IL gating (Fig. 5a). These results are consistent with the highly anisotropic oxygen transport in VO₂ that only takes place along [001] oriented channels, so that, for these (001) oriented films, there is little lateral transport. In contrast, oxygen transport in La₀.₄₅Sr₀.₅₅MnO₃ is known to be take place along all three principal crystallographic directions. In this case we find that the initially highly resistant film becomes conducting not only within, but well beyond the circumference of the orifices (Fig. 5b). Finally, for the films of SrCoO₂₅, a more complex conductivity pattern is found after gating with increases in conductivity well beyond the orifice as for La₀.₄₅Sr₀.₅₅MnO₃, but with a ring of highest conductivity around the edge of the orifice (Fig. 5c). The distinct conductivity patterns formed within these three oxide materials are readily compared in the 1D conductivity profiles shown in Fig. 5d–f. The evolution of the conductivity patterns with gating time are shown in Supplementary Fig. 16.

We propose that the ring of highest conductivity in SrCoO₂₅ is caused by the accumulation of oxygen at the interface between the original BM phase and the IL gate-induced perovskite phase, which is consistent with high-resolution cross-section STEM-HAADF imaging (see Supplementary Fig. 17). Two-dimensional finite element diffusion simulations were carried out to explore the origin of the IL gate-induced ring structure. The simulations are carried out within the film’s cross-section. We suppose that IL gating results in gradients in oxygen level (O-level), both perpendicular and parallel to the film surface, that will then lead to, via Fick’s second law, diffusion of oxygen. In the simulations, VO₂ and La₀.₄₅Sr₀.₅₅MnO₃ are injected, whereas for SCO, O²⁻ are injected through the orifices at a constant rate. In addition, we include a phase boundary between the BM and perovskite phases and we assume that oxygen can diffuse across this boundary only when the O-level difference across this interface exceeds a threshold value. Moreover, at the phase boundary there is likely band bending, which would account for a local excess or deficiency in oxygen concentration, leading to a modification of diffusion coefficients at the phase boundary (see Supplementary Fig. 18 and Supplementary Table 1 for more details). Typical results of this model in Fig. 5g–i are compared with the CAFM conductivity maps in Fig. 5a–c. As can be seen in Fig. 5g–i the simulations can qualitatively describe the distinct conductivity patterns for the three different oxide films. The influence of simulation parameters on the O-level is discussed in Supplementary Fig. 19. By decreasing the pattern dimensions to the nanoscale, such a method of patterned IL gating has the potential for the construction of a wide range of mesoscopic devices, such as tunneling junctions, and quantum wells, wires, and dots.

**Discussion**

We have shown that in situ TEM studies of samples subject to ion liquid gating is made possible by the manipulation of droplets of VO₂, La₀.₄₅Sr₀.₅₅MnO₃, and SrCoO₂₅ after ionic liquid gating through orifices in the resist overlaid on the sample. Gate voltages of +2.5 V for VO₂ and La₀.₄₅Sr₀.₅₅MnO₃ and -3 V for SrCoO₂₅ films were applied for 15 min. The IL and resist were then removed before CAFM measurements were carried out. Typical CAFM images of a single ori...
the IL using a standard AFM on a suitably prepared device. The very low vapor pressure makes it unnecessary to contain the IL in the TEM column unlike most other liquids. Applying this technique we observe the real-time transformation of the ordered vacancy oxygen structure of SrCoO$_2$.5 to its fully oxygenated form SrCoO$_3$. This requires a massive influx of oxygen, even though the in situ gating experiments are carried out in the high vacuum environment of the TEM column (which has a pressure of ~4 x 10$^{-9}$ mbar). This solves a longstanding controversy about the origin of the oxygen which must therefore be dissolved in the IL itself. One of the most surprising results of our studies is the highly anisotropic velocity of the phase front between the initial and final phases induced by IL gating. In both gating directions the phase front moves ~30 times faster along the oxide thin-film surface than perpendicular to the surface, which is attributed to the distinct properties of the surface.

By taking advantage of the IL gate-induced anisotropic oxygen motion we show that complex three-dimensional meso-structures, such as cylinders and rings, can be created from an exterior surface. Using simulations we show that these structures result from a combination of anisotropic oxygen migration and critical concentration oxygen gradients below which migration is suppressed. We assume that oxygen can diffuse across this boundary only when the O-level difference across the phase boundary are thus modified by AD. All the parameters used in the simulations are shown in Supplementary Fig. 18 and Supplementary Table 1.

**Methods**

**Sample preparation.** SrCoO$_2$.5 thin films, 40 nm thick, were grown on 10 x 10 mm$^2$ SrTiO$_3$ and NSTO (001) substrates at 750 °C, in an oxygen pressure (p$_O$) of 5 x 10$^{-4}$ mbar, using PLD. Twenty nanometer thick (001) oriented VO$_2$ films were grown at 400 °C on 0.5 wt% Nb-doped TiO$_2$ substrate at p$_O$ = 1.9 x 10$^{-2}$ mbar, while 20 nm thick (001) oriented La$_{0.25}$Sr$_{0.75}$MnO$_3$ films were grown at 600 °C on NSTO with p$_O$ = 2.0 x 10$^{-1}$ mbar. After deposition, the SrCoO$_2$.5 and VO$_2$ films were cooled to room temperature in the same oxygen pressure as used for the growth, whereas 500 mbar O$_2$ was used for cooling the La$_{0.25}$Sr$_{0.75}$MnO$_3$ films. All the data presented in this article are from samples prepared from the same wafer in each case, except for the CAFM results. The IL NW-dihydrate-N-(2-methoxyethyl)-N-methylammonium bis(trifluoromethylsulfonyl)-imide (DEME-TFSI), was used for all gating experiments. The IL and the devices were separately baked at 130 °C for all gating experiments. The IL and the devices were separately baked at 130 °C and 500 mbar O$_2$ was used for cooling the La$_{0.45}$Sr$_{0.55}$MnO$_3$ samples. A O$_2$ concentrator source with a rate of 20 μl/min was introduced to simulate the IL gating effect of negative and positive VO$_2$ respectively. The initial BM SCO phase is converted in our model to the perovskite phase when the local normalized O-level exceeds 0.5 (corresponding to x = 2.75 for SrCoO$_2$.5), giving rise to a BM/perovskite boundary in the simulation. We assume that oxygen can diffuse across this boundary only when the O-level difference across the interface exceeds a threshold value $\delta$. At the phase boundary there is likely band bending, which will lead to a local excess or deficiency in oxygen concentration. We, thus, assume, will lead to an asymmetry in oxygen transport across the phase boundary and the diffusion coefficients at the phase boundary are thus modified by $\delta$. All the parameters used in the simulations are shown in Supplementary Fig. 18 and Supplementary Table 1.

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

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Author contributions

B.C. prepared the samples. B.C. and P.W. carried out the in situ TEM measurements. T. M. and B.C. did the simulations. Z.W. carried out the out situ STEM, EELS, and EMCD under the supervision of X.Z. B.C. carried out all the other measurements. S.S.P.P. conceived and directed the project. All authors participated in discussing the data and writing the manuscript.

Additional information

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