Electronic Supplementary Information

Enhanced electrocatalytic activity via phase transitions in strongly correlated SrRuO$_3$ thin films

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Experimental detail

Thin film growth and structural characterization

High-quality epitaxial SrRuO$_3$ thin films were grown on TiO$_2$-terminated SrTiO$_3$ (for optical experiments) and 0.5 wt% Nb-doped SrTiO$_3$ (for Oxygen evolution reaction (OER) analyses) substrates using pulsed laser epitaxy (PLE). A KrF excimer laser ($\lambda = 248$ nm; Lightmachinery, IPEX 864) with a fluence of $\sim 1.5$ J cm$^{-2}$ and repetition rate of 2 Hz was used for the ablation of a sintered target. The substrate temperature was fixed at 700 °C with varying $P$(O$_2$) ranging from $3 \times 10^{-1}$ to $1 \times 10^{-4}$ Torr. The vertical distance between the target and the substrate was fixed to 65 mm. Crystalline structures of the thin films were determined using high-resolution X-ray diffraction (XRD, Rigaku SmartLab). The thicknesses of films were fixed at $\sim 30$ nm, as measured by X-ray reflectometry (XRR) (Fig. S1(a)). Figs. S1(b) and S2 show XRD $\theta$-2$\theta$ scans and rocking curves of the thin films grown at different $P$(O$_2$). The results indicate well-oriented single-crystalline thin films without any secondary phases and good crystalline quality (FWHM $\leq 0.02^\circ$). An atomic force microscope (AFM, Park Systems NX10) with a Si probe tip (Budget sensors ContAl-G) was used to confirm the surface topography (inset of Fig. S2). Root-mean-square (RMS) roughnesses of 0.687 and 0.821 nm were obtained for the SrRuO$_3$ thin films grown above ($P$(O$_2$) = $3 \times 10^{-2}$ Torr) and below ($P$(O$_2$) = $1 \times 10^{-2}$ Torr) $P_c$(O$_2$), respectively, indicating atomically flat surfaces with preserved step-and-terrace atomic structures of the substrate for both samples. Fig. S3 shows {204} SrTiO$_3$ Bragg reflections with $\varphi$ angles of 0, 90, 180, and 270°. The parameter of the SrRuO$_3$ orthorhombic unit cell parameter of $a \neq b \neq c$ and $\alpha \approx \beta \approx \gamma \approx 90^\circ$ with additional distortion can be calculated to the pseudocubic unit cell ($a_{pc} = a_{STO}$, $b_{pc} = a_{STO}$, $c_{pc}$) through the following relationships,

$$a_{pc} = \frac{c_o}{2},$$
Table S1 shows the calculated lattice parameters of SrRuO₃ thin films on SrTiO₃ substrates grown at various $P(O_2)$.

**Fig. S1.** XRR and XRD $\theta$–$2\theta$ scans for SrRuO₃ thin films on SrTiO₃ substrates grown at different $P(O_2)$. (a) XRR results show that SrRuO₃ thin films have thickness of ~30nm. (b) XRD results indicate single-crystalline SrRuO₃ thin films are grown over a wide range of $P(O_2)$ without any secondary phases.
Fig. S2. Rocking curve scans and atomic force microscopy images of epitaxial SrRuO$_3$ thin films. Rocking curve scans of (a) SrTiO$_3$ substrate, SrRuO$_3$ thin film with (b) orthorhombic and (c) tetragonal structures. Both the AFM images in the insets show the step-and-terrace structure.

Fig. S3. Off-axis X-ray diffraction for the orthorhombic and tetragonal SrRuO$_3$ thin films. (20L)$_{pc}$ XRD reflections of SrRuO$_3$ thin films grown at $P(O_2) = (a) 3 \times 10^{-2}$ and (b) $1 \times 10^{-2}$ Torr, around the SrTiO$_3$ (204) Bragg reflections with configuration of $\varphi = 0, 90, 180,$ and $270^\circ$. 
<table>
<thead>
<tr>
<th></th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$\gamma$ (°)</th>
<th>$a/b$</th>
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<tr>
<td>Bulk</td>
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<td>5.530</td>
<td>7.845</td>
<td>90</td>
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<td>7.810</td>
<td>89.020</td>
<td>1.00794</td>
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<td>7.986</td>
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</table>

**Table S1.** Lattice parameters of SrRuO$_3$ thin films grown at various $P$(O$_2$).

**X-ray photoemission spectroscopy**

The chemical structure was studied at room temperature using XPS (Theta Probe, Thermo) with a monochromated Al-$K\alpha$ X-ray source ($h\nu = 1486.6$ eV). The step size was 0.1 eV at a pass energy of 50.0 eV with a 400 $\mu$m spot size. All the peak positions were calibrated using the C 1$s$ photoemission signal (284.5 eV). In order to analyze the spectra in detail, we deconvoluted the peaks using a mixed Gaussian-Lorentzian function.$^6$

**Ellipsometry**

The optical properties of the SrRuO$_3$ thin films were investigated using spectroscopic ellipsometers (VASE and M-2000, J. A. Woollam Co.) at room temperature. The optical spectra were obtained between 0.74 and 5.5 eV for incident angles of 70 and 75°. A two-layer model (SrRuO$_3$ thin film on SrTiO$_3$ substrate) was sufficient for obtaining physically reasonable spectroscopic dielectric functions of SrRuO$_3$ that reproduced the literature spectrum.
**Theoretical calculation**

The calculations were performed using the projector augmented-wave method\(^7\) and the generalized gradient approximation exchange-correlation functional\(^8\) with a Hubbard-\(U\) correction, as implemented in the Vienna ab initio simulation package.\(^9\) The electronic wave functions were described using a planewave basis set with an energy cutoff of 400 eV. A rotationally invariant \(+U\) method\(^10\) was applied to the Ru 4\(d\) (\(U_{\text{eff}} = 2.1\) eV) orbitals, the value for which was used in previous literature.\(^11,12\) The calculations for vacancy defects in SrRuO\(_3\) were performed using 160-atom supercells. The wavefunctions were expanded in a plane-wave basis set with an energy cutoff of 400 eV, and integrations over the Brillouin zone were carried out using the \(4 \times 4 \times 2\) \(k\)-point mesh. The atomic coordinates were relaxed until the force acting on each atom was reduced to less than 0.05 eV Å\(^{-1}\). The formation energy of each vacancy was evaluated by the equation in a reference,\(^13\) by considering the secondary phases of SrO and RuO\(_2\). As an estimate for the sample growth, we set the oxygen chemical potentials (\(\mu_O\)) to \(-1.39\) and \(-1.58\) eV, corresponding to \(P(O_2)\) values of \(10^{-1}\) and \(10^{-3}\) Torr, respectively at a temperature of 700 °C.

Theoretical calculation of the vacancy formation energy supports the elemental vacancy engineering of the crystal structure. As shown in Table S2, vacancies are likely to form in the tetragonal SrRuO\(_3\), and the RuO vacancy may predominantly prevail due to it having the lowest formation energy, which is consistent with the spectroscopic observations. For an orthorhombic structure, the formation of the vacancies would be relatively suppressed since the formation energy is much higher compared to that of tetragonal SrRuO\(_3\).
Table S2. Formation energy of different types of vacancies in SrRuO$_3$ thin films with distinctive crystal structures. Theoretical calculation of formation energy (in eV) suggests that O and RuO vacancies spontaneously form in the tetragonal SrRuO$_3$ thin films, while the formation energy in the orthorhombic structure is positive for all the types of defects studied.

<table>
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<th>Vacancy type</th>
<th>Tetragonal structure (eV)</th>
<th>Orthorhombic structure (eV)</th>
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<tr>
<td>Ru</td>
<td>0.30</td>
<td>0.54</td>
</tr>
<tr>
<td>O</td>
<td>-0.19</td>
<td>1.55</td>
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<tr>
<td>RuO</td>
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In order to estimate the contribution of defects compared to that of the structural phase transition, we calculated the density of states (DOS) of stoichiometric orthorhombic SrRuO$_3$ (Fig. S4(a)), stoichiometric tetragonal SrRuO$_3$ (Fig. S4(b)), and RuO defect-induced tetragonal Sr$_{32}$Ru$_{31}$O$_{95}$ (Fig. S4(c)). The main modifications in the electronic structure indicated by optical spectroscopy are represented by red and green arrows: The occupied O 2$p$ level decreases (red) and the unoccupied Ru 4$d$ $e_g$ level increases (green) when the crystal structure changes from orthorhombic to tetragonal. Interestingly, the DOS of the stoichiometric (Fig. S4(b)) and the RuO deficient (Fig. S4(c)) tetragonal SrRuO$_3$ have the same features in terms of the main electronic structure, indicating that the structural phase transition is a crucial factor for the electronic structure modification in the SrRuO$_3$ grown at low $P$(O$_2$). In other words, elemental vacancies do not sufficiently contribute to changes in the electronic structure.
Fig. S4. Theoretical calculations of the density of states for the SrRuO$_3$ thin films. (a) Orthorhombic stoichiometric SrRuO$_3$, (b) tetragonal stoichiometric SrRuO$_3$, and (c) tetragonal RuO deficient Sr$_{32}$Ru$_{31}$O$_{95}$ thin films are shown for comparison.
Resistivity measurements

Resistivity as a function of temperature, $\rho(T)$, was measured using a low-temperature closed-cycle refrigerator (ARS-4HW, Advance Research Systems). The measurements were performed from 300 to 20 K, using the Van der Pauw method with In electrodes and Au wires.

**Fig. S5.** Changes in the electronic properties of SrRuO$_3$ thin films. Resistivity as a function of temperature ($\rho(T)$) is shown for the SrRuO$_3$ thin films deposited at various $P$(O$_2$). With decreasing $P$(O$_2$), overall $\rho(T)$ increases which could be attributed to vacancy scattering.
**Electrochemical measurements**

A Vertex potentiostat (Ivium Technologies) was used for electrochemical measurements using the three-electrode method. Ag/AgCl (reference electrode), Pt mesh (counter electrode), and high-quality epitaxial SrRuO$_3$ thin films (working electrode) were used as the electrodes. The SrRuO$_3$ films were contacted with copper wires using silver epoxy (TED PELLA, INC.) and there was no noticeable contact resistance between samples and wires. The sample, except for the SrRuO$_3$ film surface, was sealed by coating PMMA, to avoid direct exposure of the conducting substrate to the electrolyte. We carefully soaked the SrRuO$_3$ thin films into the electrolyte below the contact region and the area of the working electrode was $4.5 \times 4.5 \text{ mm}^2$. The schematic diagram of the sample for electrochemical measurements is shown in Fig. S6. For the electrolyte, we used 1 M KOH prepared with deionized water, and the same amount of the surface areas of each sample was carefully soaked into the KOH solution, without submerging the contact region. The sweep rate for cyclic voltammetry was 5-50 mV s$^{-1}$. The trends of the OER activity between the orthorhombic and tetragonal SrRuO$_3$ thin films were the same, independent of the sweep rate. Note that the potential is shown vs. a reversible hydrogen electrode (RHE).

In order to confirm that the large increase in the current level in cyclic voltammetry originates indeed from OER, we performed several additional experiments. First, as shown in Fig. S7, we confirmed that the Nb:SrTiO$_3$ substrates do not affect the OER activity of SrRuO$_3$ thin films. Second, we measured several cyclic voltammetry curves at different potential sweep range to confirm the stability. Fig. S8 shows the reversible current-potential curves in SrRuO$_3$ thin films at lower potential range (initial stability test). These measurements have been conducted on all of our SrRuO$_3$ thin films to confirm the sample are stable at low potential ($\leq 1.3 \text{ V}$), which is well above the onset potential of OER ($\sim 1.25 \text{ V}$). The data of Fig. 5 in the main text have been taken.
after these measurements. Based on this result, we believe that the low onset potential in tetragonal SrRuO₃ is due to the electrocatalytic reaction, and not coming from the materials oxidation. Third, Fig. S9(a) again shows reversible cyclic voltammetry sweep at low potential (≤ 1.3 V). These samples have been further tested using XRD to confirm that there is no change in the thickness or crystal structure of the thin films after several cycles of the electrochemical experiments. X-ray photoemission spectroscopy (XPS) shown in Fig. S10 also suggests that our samples are stable at low potential (≤ 1.3 V). We further performed the inductively coupled plasma-mass spectroscopy (ICP-MS) and we did not observe any noticeable Sr and Ru dissolution in KOH solution after the stability test up to 1.3 V for several cycles (Fig. S11). Indeed, we observed only small amount (~2 ppb) of Sr in the solution which was comparable to the reference solution and did not observe any Ru in the test solution (up to 1.3 V), for both orthorhombic and tetragonal SrRuO₃ thin films. We also show the solution after applying potential up to 1.7 V for comparison, where the elements (both Sr and Ru) are actually dissolved into the solution. Fig. S12 shows the chronoamperometric measurements as compared with cyclic voltammetry. While the SrRuO₃ thin film is known to dissolve in alkaline solution at a large applied voltage (> 1.5 V), current density well above the onset potential (up to ~1.4 V) is maintained, indicating consistent OER behavior.

Fig. S13 shows the Tafel plots for all the SrRuO₃ thin films with slope values of (i) 1 × 10⁻¹ Torr: 77.7 mV dec⁻¹, (ii) 3 × 10⁻² Torr: 66.2 mV dec⁻¹, (iii) 1 × 10⁻² Torr: 107.4 mV dec⁻¹, (iv) 3 × 10⁻³ Torr: 108.5 mV dec⁻¹, and (v) 1 × 10⁻⁴ Torr: 106.1 mV dec⁻¹, respectively. Again, a clear distinction is demonstrated, indicating the difference in the kinetics of the OER between the SrRuO₃ thin films with different crystalline structures (orthorhombic and tetragonal).
**Fig. S6.** Schematic diagram of SrRuO$_3$ thin film sample for the electrochemical measurements.

**Fig. S7.** Current-potential curves of SrRuO$_3$ thin film and Nb:SrTiO$_3$ substrate. Nb:SrTiO$_3$ substrate does not show any current in the whole potential range, which allows us to eliminate the contribution of the substrate to the observed OER activity in the SrRuO$_3$ thin films.
**Fig. S8.** The current-potential cycle in (a) orthorhombic and (b) tetragonal epitaxial SrRuO$_3$ thin films at lower potential range (initial stabilization test). The Figure shows the data with a scan rate of 50 mV s$^{-1}$, but the same systematic trend is observed for the same measurements with lower scan rates (5-50 mV s$^{-1}$).

**Fig. S9.** Reversible cyclic voltammetry results at low potential range (< 1.3 V) of (a) orthorhombic and (d) tetragonal SrRuO$_3$ thin films. (b,c,e,f) XRD result for the SrRuO$_3$ sample before and after the initial stability test. Gray lines indicate pristine SrRuO$_3$ thin film and color lines indicate the same sample after the initial stability test, respectively.
**Fig. S10.** X-ray photoemission spectroscopy for (a) orthorhombic and (d) tetragonal SrRuO$_3$ thin films before and after the initial stability test, respectively.

**Fig. S11.** Contents of dissolved elements in the KOH solution obtained by ICP-MS. Our results show negligible amount of dissolution of the sample both orthorhombic and tetragonal structure when the potential is applied up to 1.3 V, which is clearly higher than the onset potential of OER.
**Figure S12.** Chronoamperometric measurements on the orthorhombic and tetragonal SrRuO$_3$ epitaxial thin films grown at $3 \times 10^{-2}$ and $1 \times 10^{-2}$ Torr, respectively, in dark.

**Fig. S13.** Tafel plots of epitaxial SrRuO$_3$ thin films grown at different $P$(O$_2$). Tafel plots show the tetragonal SrRuO$_3$ films have smaller overpotential than orthorhombic SrRuO$_3$ films.
References


