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**Supporting Information for Direct Identification of Dynamic Reconstructed
Active Phase of Perovskite LaNiO_3 under Oxygen Evolution Reaction**

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Epitaxial growth of LaNiO₃

LaNiO₃ (LNO) films were epitaxially grown on 0.7% Nb doped SrTiO₃ (Nb-STO) substrates by pulsed laser deposition (PLD). The films were grown at a repetition rate of 5 Hz and energy density of 2J/cm² with 248 nm KrF excimer using an LNO target. The thickness of film was ~ 35 nm. The commercial 99.99% element purity LNO target used was purchased from KJMTI Company. The target surface was cleaned by laser to avoid impurities before deposition. The substrates were heated to growth temperature with a heating rate of 25°C/min, and oxygen pressure was kept at 15 mTorr during growth process. We varied growth temperature to tune the surface termination. Ni-rich termination LNO was deposited under 450°C and the growth temperature of La-rich termination LNO is 750°C. After deposition, all films were annealed at growth temperature under pure O₂ (200 mTorr) for 30 min to ensure full oxidation.

Characterizations of single crystal thin films

The crystal and epitaxial relationship were determined by high resolution X-ray diffraction (XRD) with Cu K α radiation. It used a PANalytical four-circle diffractometer in $\theta - 2\theta$ scans. LNO (001) and (002) peaks have been exhibited in Figure S1. And atomic force microscope (AFM) was performed by NanoWizard (JPK instruments).

Angle resolved X-ray photoelectron spectroscopy (ARXPS) was carried out by using a Quantum 2000XPS equipped with a monochromatic Al K α (1486.6 eV) X-ray source, to obtain the core level and valance band structure spectra of all samples. The core level spectra were subtracted by a Shirley-type background. And the binding energy calibration was performed by using gold (Au) standard samples by setting Au 4f 7/2 peak at binding energies of 83.96 ± 0.1 eV respectively. The XPS spectra were performed at different emission angles θ from 0° to 60° with respect to the sample surface stage.

Cyclic voltammetry details

The electrochemical experiments were carried out in a three-electrode electrochemical cell. Cyclic voltammetry (CV) was performed with CHI 760E. The electrolyte was pH=13 alkaline solution prepared by KOH (99.999%) and ultra-pure water (18.2 M Ω ·cm, Milli-Q), and the working electrode was Ni- and La-rich termination LNO single crystal films. The reference electrode Hg/HgO (0.1M KOH) and counter electrode platinum were used.

EC-STM setup

Electrochemical scanning tunneling microscopy (EC-STM) measurements were carried out on a Multimode VIII STM instrument (Bruker, Santa Barbara, CA) under constant current mode. The EC-STM tips used were mechanically cut from a Pt/Ir wire (Pt80/Ir20; $\phi=0.25$ mm) and insulated by thermosetting polyethylene to reduce Faradaic current. In the EC-STM cell, the working electrode was Ni- and La-rich termination LNO freshly prepared before each experiment, and the counter electrode was Pt wire. The electrolyte was pH=13 alkaline solution, which is same as the electrolyte in CV setup. The reference electrode used was homemade Au/AuO quasi-reference electrode. The STM electrochemical cell was made of Teflon and exposed a sample area of 0.48 cm² to the solution through an O-ring. The measured tip current before engaging was less than 0.01 nA. All STM images were recorded in the constant current mode at typical tunneling set-point current of 1 nA. The potential of tip was 0.87 V vs RHE with iR correction and the sample potential was ranging from 1.12 to 1.72 V vs. RHE with iR correction. The constant scan rate conducted in EC-STM was 2 Hz with 256 points per line. The height diagram of STM images were analysed by NanoScope Analysis 2.0.

Normalization of ARXPS

The areas of the spectra in ARXPS of Figure 2 are normalized to the peak area of specie which has highest concentration on the surface. For example, for the Ni-terminated LNO, the areas of spectra are normalized to the area of Ni 3p peak. And for the La-terminated LNO, the areas of spectra are normalized to the area of La 4d peak.

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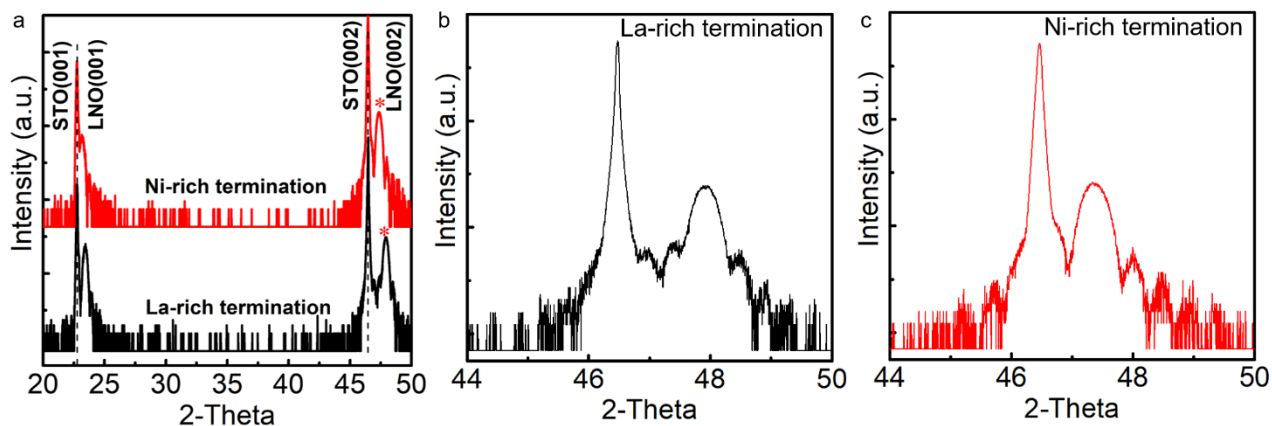


Figure S1. (a) XRD θ - 2θ scans of the LNO films grown on Nb-STO substrates. The red stars mark the (002) Bragg peaks of the epitaxial films. And zoom-in image around (002) with Laue fringes of (b) La-rich terminated LNO, (c) Ni-rich terminated LNO.

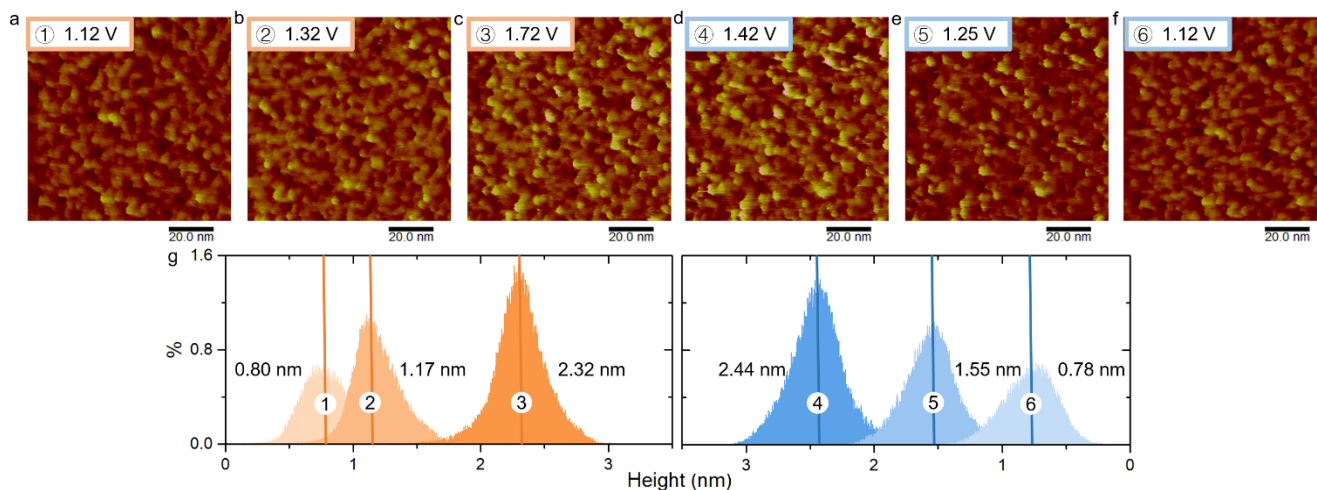


Figure S2. EC-STM images measured in forward CV scans at applied potentials of (a) 1.12 V, (b) 1.32 V, (c) 1.72 V, and backward CV scans at (d) 1.42 V, (e) 1.25 V, (f) 1.12 V with the size of $90 \times 90 \text{ nm}^2$. (g) The depth histograms of EC-STM images at different potentials, respectively. The potential applied to the Pt/Ir tip was kept at 0.87 V and all the potentials here are versus RHE. The tunnelling current was 1 nA.

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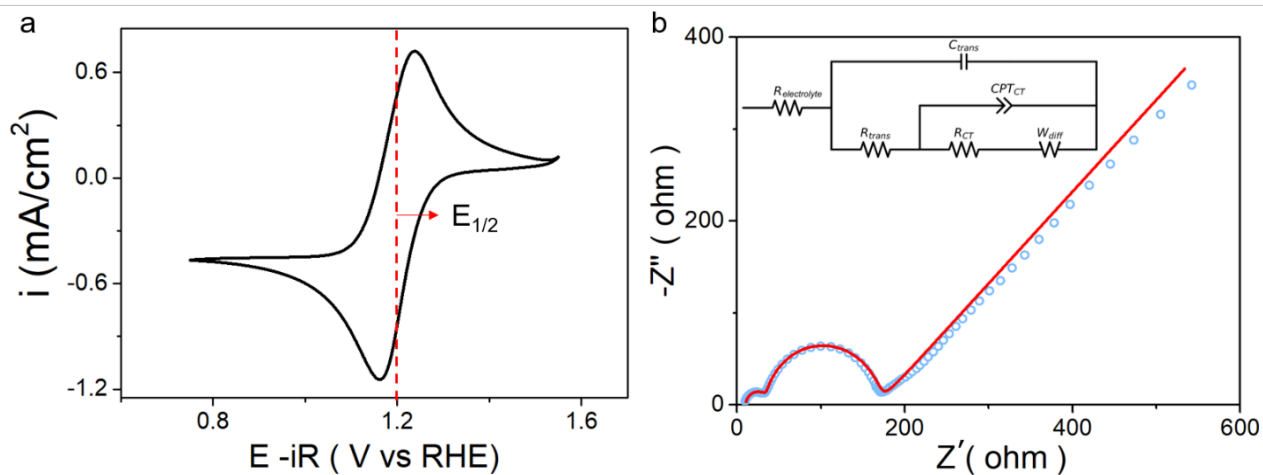


Figure S3. (a) CV at a scan rate of 10 mV/s in 0.1 M KOH, N_2 -saturated with 5 mM each $[Fe(CN)_6]^{3-/4-}$ for LNO on Nb-doped STO. (b) Electrochemical impedance spectroscopy (EIS) at $E_{1/2}$ (1.2 V vs RHE). The inset image is model for fitting.

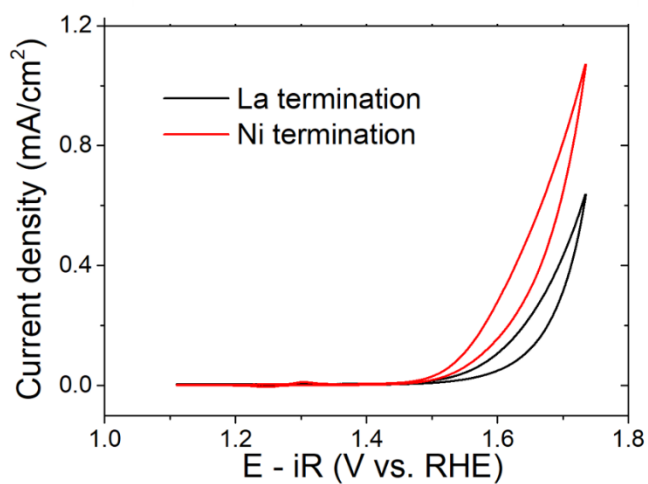


Figure S4. CVs at 10 mV/s of Ni-rich termination and La-rich termination LNO in separate cell. Counter electrode is Pt. The applied potential is referenced to RHE with iR correction.

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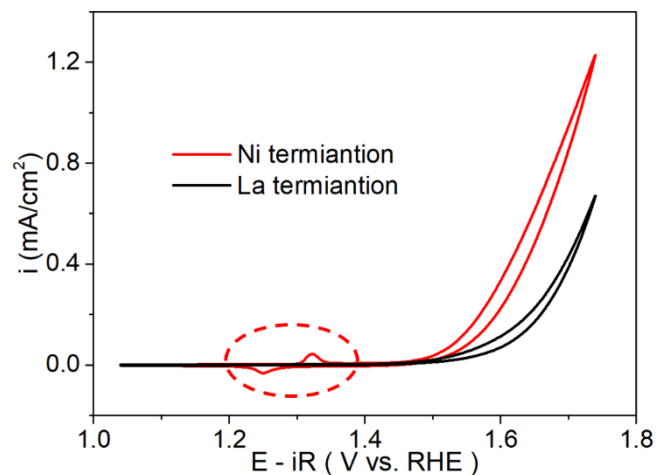


Figure S5. CVs at 10mV/s of Ni-rich termination and La-rich termination LNO in EC-STM cell. Counter electrode is Pt. The redox peaks are highlighted with red dot circle. The applied potential is referenced to RHE with iR correction.

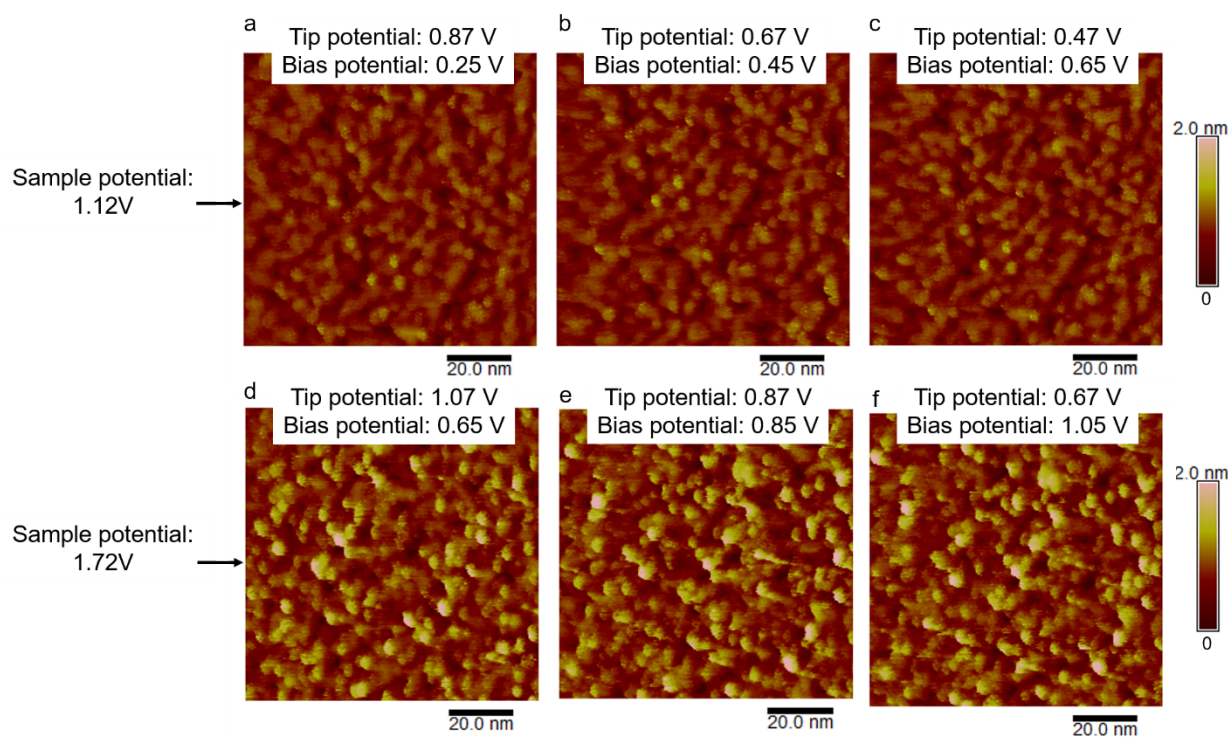


Figure S6. EC-STM images measured at applied potentials of 1.12 V and tip potentials of (a) 0.87 V, (b) 0.67 V, (c) 0.47 V. EC-STM images measured at applied potentials of 1.72 V and tip potentials of (d) 1.07 V, (e) 0.87 V, (f) 0.67 V.

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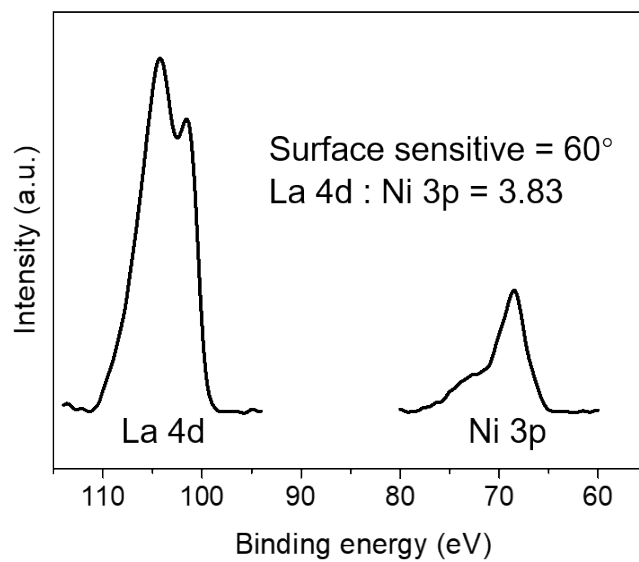


Figure S7. La 4d and Ni 3p core-level spectra at $\theta=60^\circ$ for Ni-rich terminated LNO after OER by ARXPS. The La/Ni ratio is 3.83, which is smaller than that before OER with a value of 4.51 in Figure 2b.