

Supporting Information for Charge transfer induced O *p*-band center shift for an enhanced OER performance in LaCoO₃ film

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Detailed Experimental Section:

The Film Fabrication.

High quality epitaxial thin film of LaCoO₃ (LCO) and influence layer include La_{0.67}Sr_{0.33}MnO₃ (LSMO) and La_{0.7}Ca_{0.3}MnO₃ (LCMO) were fabricated by pulsed laser deposition (PLD) on single crystal (100)-oriented Nb:SrTiO₃ (Nb:STO) substrates. The PLD target of LaCoO₃ was synthesized by a normal solid-state reaction from stoichiometric mixtures of La₂O₃ and Co₃O₄ powder¹³The mixtures was pressed into a pill and sintered at 1350°C. The other targets were purchased from MTI (Hefei, China). A total of 20000 pulses of LSMO or LCMO was deposited at a pulse frequency of 2 Hz and 700 °C under 100 mTorr O₂ as the influence layer between LCO and Nb:STO. Then a total of 5000 pules of LCO were deposited at the same condition.

HRTEM and SEM Measurements.

The HRTEM sample is prepared by Helios NanoLab 600i. W metal is deposited on the top of La_{0.67}Sr_{0.33}MnO₃ aiming to protect the La_{0.67}Sr_{0.33}MnO₃ from the ion milling. And Pt ion beam etching is used to remove the amorphous layer after the ion milling. As a result Pt particles are left on the sample, which do not affect the measurement. HRTEM data is measured by Tecnai G2 S-Twin F20. SEM data is measured by Helios NanoLab 600i.

Electrochemical Measurements.

The current-voltage (I-V) characteristic curves were obtained from a sweeping current-potentiometric scans (LSV) using CHI660E electrochemical workstation (CH Instruments Ins, America). The measurements were performed using a three electrode system. A platinum electrode was used as a counter electrode. As the potential was reported against the reversible hydrogen electrode (RHE) a silver chloride electrode (Ag/ AgCl) was used as a reference electrode:

$$E_{\text{RHE}} = E_{\text{AgCl}} + 0.059\text{pH} + E^0_{\text{AgCl}}, \text{ with } E^0_{\text{AgCl}} = 0.1976 \text{ V at } 25^\circ\text{C}. \quad (1)$$

The measurements were performed under 0.1M KOH, 25°C, at a scan rate of 5mV s⁻¹ between 1.2 V_{RHE} and 1.9 V_{RHE}. After the characterization, a thin film was attached to an iron pill then covered by with an inert glue leaving a certain surface area as a working electrode (details for the electrode see Supporting Information Figure S5).

Electrochemical impedance spectroscopy measurements (EIS) were performed using a CHI660E electrochemical workstation (CH Instruments Ins, America). The frequency range was from 0.1 Hz to 1M Hz. The measurements were performed at room temperature at a potential range of 1.4 V_{RHE} and 2.0 V_{RHE}.

XPS Measurements.

A Thermo ESCALAB250 XPS was used to collect the binding energies of core level of O and Co with the X-ray excitation source of Al K α (1486.6 eV). The valence band spectrums were also collected to further study the electronic structure of LaCoO₃ near the Fermi level.

HRTEM and SEM data

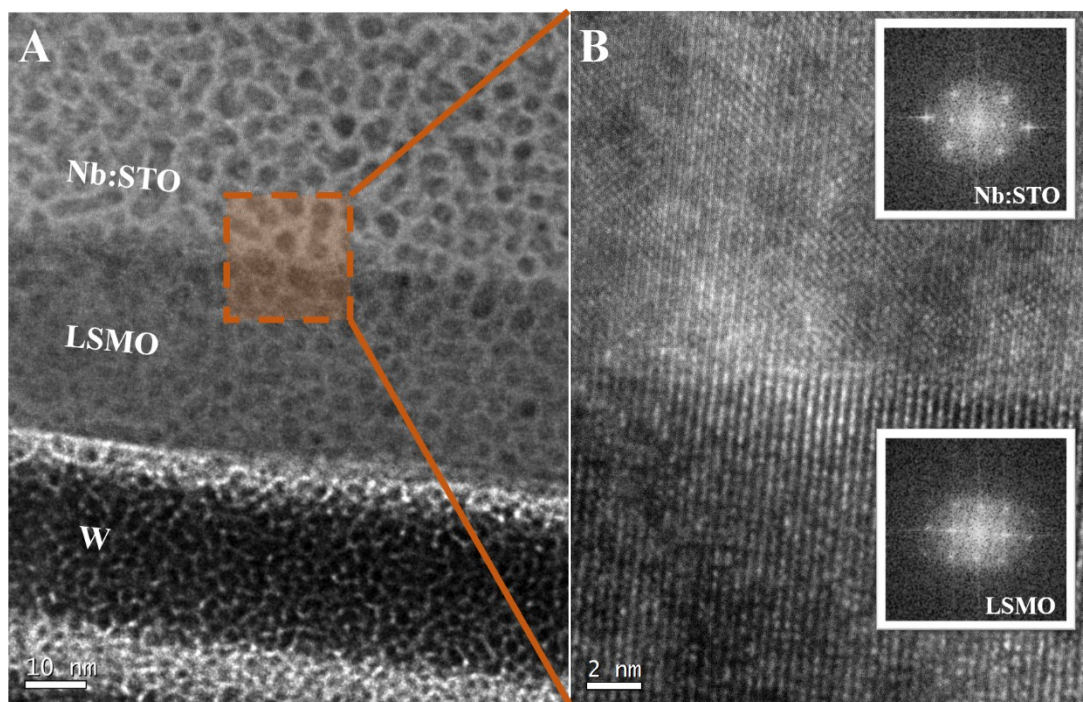


Figure S1. A HRTEM image for epitaxial $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ thin film grown on the Nb:STO (001) substrate. B Magnified images for near the interface between $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ and Nb:STO. Insets show the FFT patterns for $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ and Nb:STO.

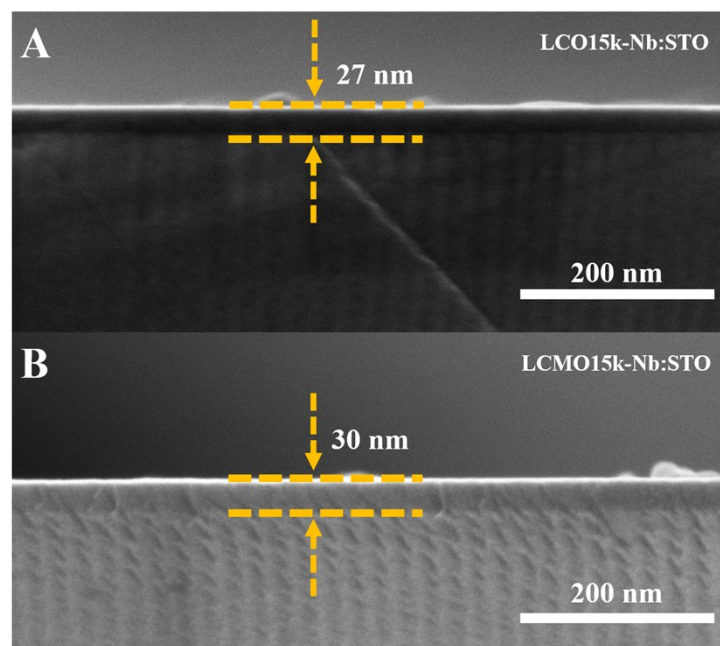


Figure S2 A. SEM image for epitaxial LaCoO_3 thin film grown on the Nb:STO (001) substrate. B. SEM image for epitaxial $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ thin film grown on the Nb:STO (001) substrate.

LSV data

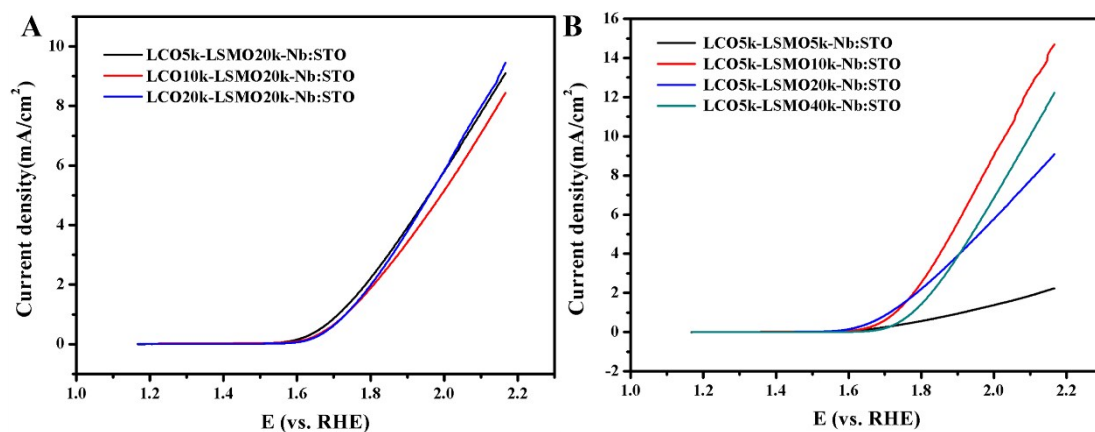


Figure S3. A. Linear Sweep Voltammetry (LSV) for the different films with different thickness of LaCoO₃. B. Linear Sweep Voltammetry (LSV) for the different films with different thickness of La_{0.67}Sr_{0.33}MnO₃

XPS data

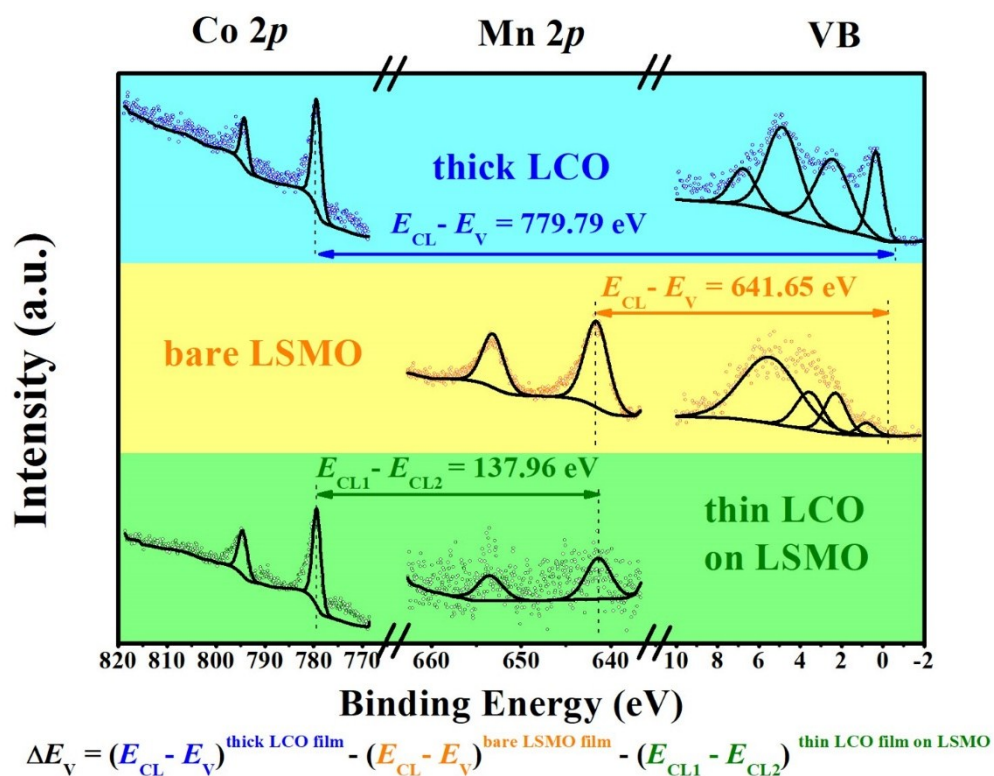


Figure S4 A schematic illustration shown how the VBO is calculated by XPS. LCO20K-LSMO20K-Nb:STO, LSMO20K-Nb:STO, LCO5K-LSMO20K-Nb:STO are used as the thick LCO, bare LSMO, thin LCO sample, respectively.

O 1s and Co 2p:

The O 1s spectrum shows four features at ~528.8, ~529.5, ~531.4 and ~533.2 eV shown in Fig. S3 A. The peak at ~528.8 eV can be assigned to the bulk lattice oxide peak. The peak at ~529.5 eV can be attributed to surface hydroxylation that has been reported previously.¹ The broad peak at ~531.4 eV can be related to the oxide surface species include under coordinated in the crystal terminal plane or adsorbed oxygen on the surface. The last peak at ~533.2 eV is related adsorbed water on the surface. By integrating the peak area listing Table S2, there are not obvious differences among the samples. The Co 2p spectrum which shows a normal Co³⁺ feature is shown in Fig. S3 B.

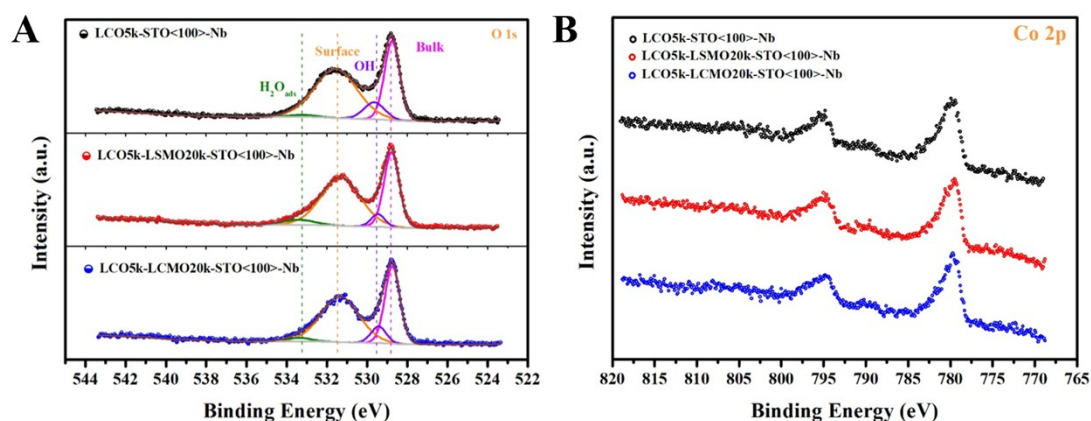


Figure S5. A. The O 1s spectrum B. The Co 2p spectrum

Sample	Area Ratio					All	Percent _{Surface} (%)
	Bulk	Surface	OH	H ₂ O _{ads}			
LCO5K	0.58	1.00	0.17	0.03	1.78	56.18	
LCO5K-LSMO20K	0.61	1.00	0.09	0.09	1.79	55.86	
LCO5K-LCMO20K	0.67	1.00	0.14	0.05	1.86	53.76	

Table S1. The fitting results of O 1s spectrum.

The electrode structure and the circuit configuration

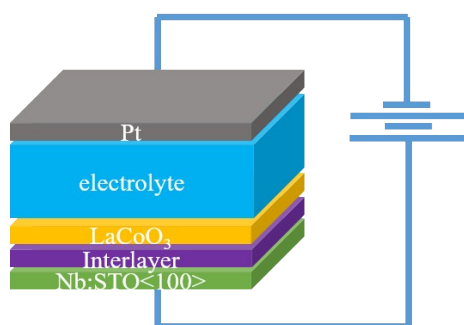


Figure S6. The electrode structure and the circuit configuration.

EIS data fitting Results:

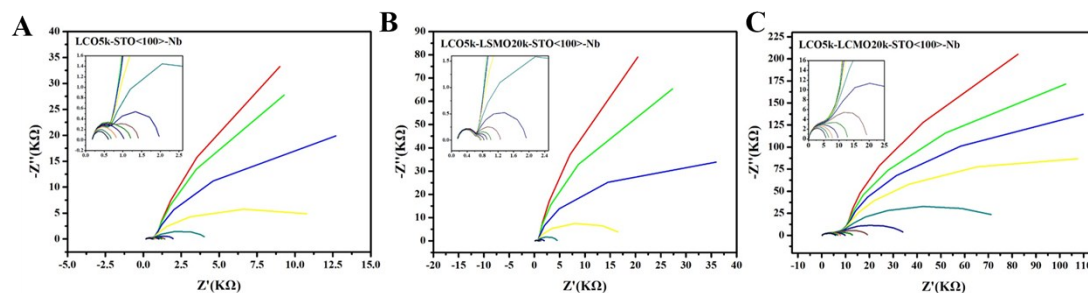


Figure S7 The initial EIS data of the three LCO samples.

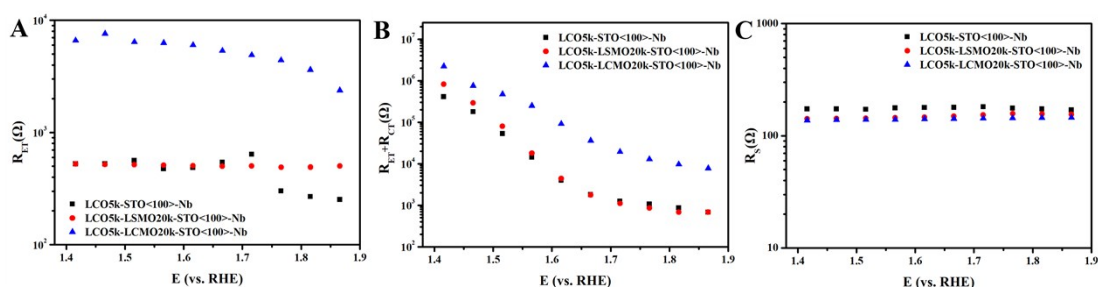


Figure S8 A. The R_{ET} values as a function of applied potential. B. The $R_{ET} + R_{CT}$ values as a function of applied potential. C. The R_S values as a function of applied potential.

R_S is the series resistances include the resistances of the substrate Nb:STO and the external contact resistances (e.g. the iron pill connections and the electrolyte resistances), shown in Figure S7 C. These resistances are used to compensate in the current density-voltage characteristics. The plot of the series resistances with applied potential is almost a straight line, due to the series resistances are not depended on the applied potential. And the series resistances of three films are very close, which will guarantee the same external contact resistances between these films.

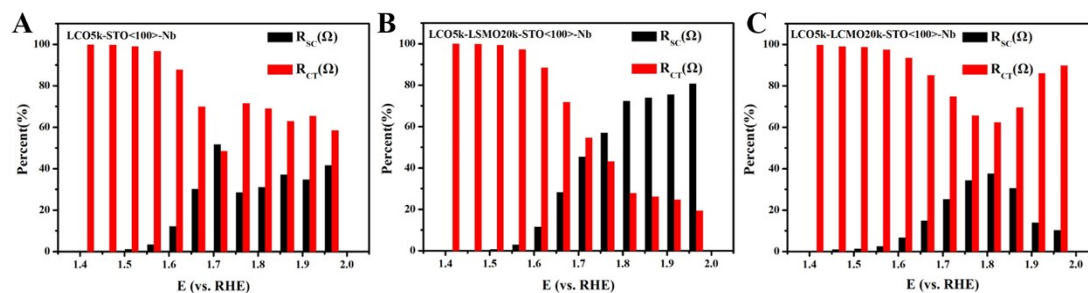


Figure S9. Three histograms are shown in 4A, 4B, 4C. They show the change of the proportion of R_{ET} values and the proportion of R_{CT} values in the sum of these resistances. It is visible before 1.7 V_{RHE} the R_{CT} values are the domination in both three films as the space charge layer and the Helmholtz layer are beginning to form. After 1.7 V_{RHE} in both LCO/Nb:STO and LCO/LCMO, the R_{CT} values are still the dominated activity parameter. However in LCO/LSMO, the R_{ET} values are the dominated activity parameter as the electron transfer resistances keeping constant.

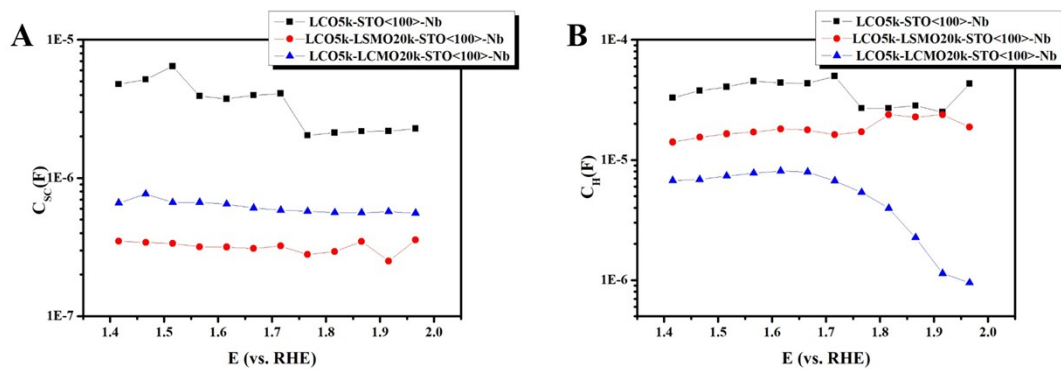


Figure S10. A, B are the capacitance of the space charge layer and the Helmholtz layer along with the applied potential respectively. As the fitting error is too large to accurate quantification. We can only make sure that the capacitances of the Helmholtz layer is much larger than the capacitances of the space charge layer during overall reaction. That means the width of the Helmholtz layer is much smaller.

References

- 1 K. A. Stoerzinger, W. T. Hong, E. J. Crumlin, H. Bluhm, M. D. Biegalski and Y. Shao-Horn, *J. Phys. Chem. C*, 2014, 118, 19733-19741.