Supplementary Information: Tunable pH-Dependent Oxygen Evolution Activity of Strontium Cobaltite Thin Films for Electrochemical Water Splitting

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S1: Additional crystallographic information and surface properties of the brownmillerite phase of the SrCoO_{2.5} (BM-SCO) thin films obtained from high resolution X-ray diffraction (HRXRD), reflectivity (XRR), Scanning Electron Microscopy (SEM) and Atomic force microscopy measurements (AFM).



Figure S1A: XRR and HRXRD rocking curve. (a) A 25 nm thick BM-SCO thin film XRR scan with its simulation. (b) Rocking curves of the BM-SCO thin films with different thickness measured across the (008) Bragg reflection, compared with that one of the LAO substrate measured across the (002) Bragg reflection. The rocking curves of the films are very similar to the substrate for the coherent component. The typical twinning domain peaks present in the rocking curve of the LAO substrate are also visible in the thinner films, as an indication of the coherent growth of the films on the substrate.

The XRR measurements were carried out to calibrate the thickness and determine the roughness

of the BM-SCO films, as can be found in Figure S1A. The experimental and theoretical reflectivity curves are shown in Figure S1A. The theoretical calculation was performed with the IMD code¹ available in the XOP package² and corresponded to the theoretical behavior of a film on a LaAlO₃ (LAO) substrate, with a thickness of 25 nm and a density of 5.18 g/cm^3 . Such simulation yielded a surface roughness of 0.5 nm, which was compatible with the values obtained from the AFM measurements.



Figure S1B: Surface morphology of thin films with different thickness obtained by SEM and AFM. The AFM result of the LAO substrate is also shown for comparison.



Figure S1C: XRD measurements of the SCO thin films having different thickness: 25 nm (left), 50 nm (center) and 100 nm (right). The blue and green lines are the peak fitting curves to extract the peak positions for the c-axis lattice parameter evaluation.

| SCO thickness (nm) | substrate | Rq (nm) | Ra (nm) |
|-----------------------|-----------|---------|---------|
| 25 | LAO | 0.805 | 0.538 |
| 50 | LAO | 0.537 | 0.406 |
| 100 | LAO | 0.724 | 0.576 |

Table S1 the surface roughness of the BM-SCO thin films

S2: Near-order characterization by Raman spectroscopy.

The BM-SCO thin film Raman spectra showed three main peaks at about 210 cm⁻¹, 270 cm⁻¹ and 660 cm⁻¹, which can be assigned to the three B_{3g} modes, and one peak at about 430 cm⁻¹, which can be assigned to the B_{2g} mode³. In addition, the peaks at about 120 cm⁻¹, 150 cm⁻¹ and 480 cm⁻¹ can be assigned to the A_g mode and two E_g modes, respectively, of the LAO substrate⁴. According to the Raman characterization reported in literature, SCO in BM phase consisted of CoO₆ octahedral and CoO₄ tetrahedral layers, the last can be considered with ordered oxygen vacancy channels³. The B_{2g} mode was related to the bending vibration of both CoO₆ and CoO₄ with the Co out-of-phase vibration along the x-axis; while the third B_{3g} mode was related to the CoO₆ breathing mode, with Co out-of-phase vibrations along the y-axis and O out-of-phase stretching in the yz-plane.

The magnified Raman spectra of 25 nm BM-SCO film is reported in Figure S2a to highlight the very weak B_{3g} modes having thickness dependent intensity signal. The position of the Raman peaks of all the BM-SCO films with different thickness is obtained by multi peak fitting of the spectra with Gaussian functions, as shown in Figure S2b.



Figure S2: Near order characterization of thin films through confocal Raman microscopy. The magnified Raman spectra of the 25 nm BM-SCO thin film from which the B_{3g} vibration modes at ~210cm⁻¹ and ~270 cm⁻¹ can be more clearly observed. (b) Fitting of the Raman spectra of the three samples with different thickness (25 nm, 50 nm and 100 nm, from the top to the bottom), as well as of the substrate (at the very bottom). All the spectra are normalized to the substrate peak intensity.

S3: Technical details of the OER activity measurements

To measure the OER activity of the different BM-SCO samples on the LAO substrate, a threeelectrode electrolyzer was assembled. As illustrated in Figure 3a, our experimental setup consists of the BM-SCO working electrode (anode), the Pt counter electrode (cathode) and the Ag/AgCl reference electrode in KOH solution. First, the Ti wire was glued to the backside of the BM-SCO sample (Figure S3a and b). The film was then inserted into the electrolyzer as anode. Cyclic waveform voltages were applied between the BM-SCO film, as working electrode, and the Ag/AgCl reference electrode. The currents were measured between the working electrode and the Pt counter electrode. In addition, a tube with 100 sccm oxygen flow was inserted into the solution to ensure the electrolyte is in O₂ saturated condition. The real test setup is shown in Figure S3c, in which the red, blue and white wires are connected to the working electrode, counter electrode and reference electrode, respectively. A small tube of 3.3 mm diameter was used to supply oxygen before reaction. In Figure S3d, a full scan of the BM-SCO films with different thickness at pH 13.0 KOH solution is reported.



Figure S3: OER activity measurements in alkaline media. (a) A prepared electrode of a BM-SCO film on the LAO substrate. A titanium wire is pasted to the back of LAO through carbon glue. (b) The back and side edges of the sample are covered with inert epoxy, thus localizing the reaction on the catalyst surface. (c) The three-electrode electrolyzer setup, which includes BM-SCO based working electrode, counter electrode and reference electrode. (d) The full OER activity measurements in a cyclic voltammetry for the different BM-SCO films at pH 13.0.

S4: X-ray absorption spectroscopy (XAS) measurements

In Figure S4 the O K-edge XAS curves (mainly $1s \rightarrow 2p$ transitions) in TFY of BM-SCO films are shown, probing the O 2p states are hybridized with the metal states. The spectra were normalized to have the same area in the energy range between 522-560 eV. For a better comparison among the different samples, the increasing background between 528.5 eV and 531 eV, shown as the solid curves, has been fitted by a combination of Gaussian and linear background and subtracted from the pre-edge region (see inset of Figure S4a for the background subtracted pre-edge signal). Considering the strong hybridization of the Co 3d states and the O 2p states, the variations in the 3d level occupation could affect the O K-edge spectra⁵⁻⁹.



Figure S4 (a) O K-edge XAS of the BM-SCO films with different thickness in Total Fluorescence Yield (TFY). The solid curves are the background curves as described in the text. (b) A comparison of the 100 nm thick BM-SCO thin film XAS spectra with different detection modes, i.e. TFY and Total Electron Yield (TEY). The spectra obtained for the LAO substrate in the same detection modes are also shown.

We also measured the XAS at the Co $L_{2,3}$ -edge, which probed the unoccupied (empty) states reachable by $2p \rightarrow 3d$ transition. The results for the BM-SCO samples with different thickness measured by TEY are reported in Figure S5A, while the comparison between TEY and TFY for a 100nm sample is reported in Figure S5B.

All XAS spectra had similar shape, which resembled that one of HS-Co^{3+ 9,10}. No relevant energy shift can be observed in all the measurements, which demonstrated that the valence state of cobalt was mainly Co³⁺ and was not significantly changing with the strain. Hence, we assumed that the OER and pH dependent properties were not a consequence of the different valence states of cobalt. The branching ratio (BR), which describes the spin state of cobalt, defined as the ratio of the L₃ and L₂ peaks, also does not significantly change among the different samples when the measurements are performed in TEY (see Figure S5a). On the contrary, the BR is much lower in TFY (see Figure S5b). As already mentioned above, by TFY the XAS measurements were much more sensitive to the strained interface and, thus, we can conclude that the BR was lower near the interface of the SCO films due of the strain effects at the interface. It was well known that the BR was proportional to the spin-state^{10,11}, but also the tetrahedral contribution could make larger the BR with respect to a pure octahedral HS-Co³⁺ ions⁹. Therefore, the BR behavior could be attribute to a reduced tetrahedral contribution close to the interface and/or a lower spin-state in our highly strained films.



Figure S5 (a) The Co L-edge XAS curves for BM-SCO films with 25, 50 and 100 nm thickness in TEY. (b) The Co L-edge XAS curves in TFY and TEY for the 100 nm thick BM-SCO film.

S5: X-ray Photoemission Spectroscopy (XPS)

To obtain information on the buried interface located several tens nanometers deep from the top surface and to get more detailed information about the strain dependent electronic and chemical state of our films, we made XPS depth profile measurements by soft Ar⁺ ion sputtering. There are mainly two advantages related to the use of Ar⁺ ion bombardment in XPS: first, we can remove the surface contaminants; second, we can realize the depth profile of the film to obtain vertical resolution in the XPS analysis. The low energy of the ions allows keeping restrained possible atomic and electronic structure modifications induced by the ion bombardment. Gentle Ar⁺ etching has been recently demonstrated to better avoid sputtering induced cation reduction and in case of cobalt no clear sputtering induced reduction was indeed observed¹²⁻¹⁴. We recorded the evolution of all the core-level spectra of a 100 nm BM-SCO film by XPS depth profile through the whole film thickness, from the top surface down to the LAO substrate. Differences in the scattering cross section and sputter yield of each element can induce variation in the chemical composition, such as reduction in oxygen stoichiometry. However, no clear change was found for the line shape of the core-level peaks, suggesting that the sputtering induced reduction can be neglected.

The results for Sr 3*d*, Co 2*p*, O 1*s*, La 3*d*, Al 2*p* core levels, as well as the area ratio of Sr/Co and (Sr+Co)/O, with different etching depth, are reported in Figure S6. The Al 2*p* spectrum indicated when the sputtering depth exceeded the film thickness and reached the LAO substrate. The stoichiometry expressed in terms of Sr/Co and (Sr+Co)/O area ratio were obtained from the Sr 3*d*, Co 2*p* and O 1*s* core levels. By XPS, we used the La $3d_{5/2}$, Al 2*p* and O 1*s* core levels of the deepest layers reported in Fig. S6 a, e and f from the LAO substrate, measured when the film core levels are completely disappeared, to obtain the instrumental factor necessary to calibrate the concentration calculation of the BM-SCO film. The substrate core levels used for the calibration were measured at the end of the etching process when all the film layers were completely removed. We can also notice in Figure S6a that the O 1*s* spectra of the LAO substrate are shifted to higher binding energy (BE) of about 2 eV with respect to the BM-SCO sample. This is possibly associated to the alignment of the chemical potentials related to the valence band discontinuity between LAO (energy gap about 5.6 eV) and BM-SCO (energy gap about 2.2 eV)¹⁵, consequent band realignments and, eventually, built-in potential. The exact origin of the chemical shift and of the band alignment is beyond the scope of our paper.

We calculated the La/Al and (La+Al)/O area ratio using the relative sensitivity factor of 0.537 for Al 2p, 28.1 for La $3d_{5/2}$ and 2.93 for O 1s. We found that a multiplicative factor of 1.22 was needed to obtain the expected values of La/Al=1 and (La+Al)/O=2/3. The same factor was then used to calibrate the concentration calculation for the BM-SCO film from the core levels of O 1s (a), Co 2p (b) and Sr 3d (c) measured at the beginning of the etching process when the substrate signal was completely absent. We ruled out the intermediate scans between the SCO and LAO layers in the calculation. We used the relative sensitivity factor of 5.05 for Sr 3d and 12.6 for Co $2p_{3/2}$. The results are reported in panel (d) with different etching depth. We can observe that the Sr/Co area ratio was about 1.06-0.94 and (Sr+Co)/O area ratio was about 0.81-0.77, very close to the expected values for the BM phase, that was 1 and 4/5 for Sr/Co and (Sr+Co)/O, respectively.



Figure S6 XPS depth profile analysis of a 100 nm thick BM-SCO film showing (a) O 1s (b) Co 2p (c) Sr 3d (e)Al 2p and (f) La 3d core level spectra. (d) Sr/Co and (Sr+Co)/O area ratio.

From a careful inspection of the Co 2p core levels we inferred that the cobalt valence state was not significantly changing. Indeed, the line shape of the Co 2p spectra with different etching depth of Fig. S6b are all quite similar to each other. The binding energy difference between the Co $2p_{3/2}$ and Co $2p_{1/2}$, which can be used to estimate the average valence state of cobalt, was not changing with the probing depth. Since in the depth profile XPS measurements we do not observe any adventitious carbon for BE calibration, we use an unclean similar sample to extract the absolute BE value of the Co $2p_{3/2}$ as reported in Figure S7a. After BE calibration with the C 1s photoemission peak at 285 eV, we obtained the maximum of Co $2p_{3/2}$ at about 780.6 eV. Such a value was compatible with both the Co²⁺ and Co³⁺ valence state taken from NIST Database¹⁶, i.e. 780 - 780.6 eV for the CoO (Co²⁺) and 780-781.3 eV for the Co₂O₃ (Co³⁺). As a consequence, the valence state of cobalt is also hardly quantified by deconvolution of the main peak of Co 2p into the different components corresponding to the different valence states. On the contrary, we use the BE difference between the Co $2p_{3/2}$ and Co $2p_{1/2}$, to estimate the average valence state of cobalt. It can be observed that such BE difference is not changing with the probing depth. As an example, in Fig. S7b we report the fit of three Co 2p core level spectra, corresponding to the etching depth of 10.8 nm, 46.8 nm and 91.8 nm. The binding energy difference between the Co $2p_{3/2}$ and Co $2p_{1/2}$ was always about 15.34 eV, which roughly corresponded to the Co³⁺ valence state¹⁷⁻²¹. The same cobalt valence state was inferred by the XAS at the Co L-edge, as reported above. The fit shown in Fig. S7b is performed including non-local and local screening contributions (labelled as A and B, respectively, in the figure) rather than different components corresponding to the different valence states. In addition, local and non-local screening contributions must also to be included in the fit of the spectra¹⁸⁻²¹. We also included the shake-up satellites resulting from the ligand-to-metal charge transfer during the photoemission process which can be interpreted, at the simplest level of approximation, by a molecular orbital description²²⁻²⁴. We kept the number of fitting components to the minimum and fixed the degeneracy ratio of 2:1 for the two spin-orbit coupling components Co $2p_{3/2}$ and Co $2p_{1/2}$. The contribution of the shake-up satellites at about 5.8 and 9.5 eV above the main peak, corresponding to Co²⁺ and Co³⁺ respectively, was also present. The satellites relative area was expected to be 33% and 9% of the total Co $2p_{3/2}$ signal for the Co²⁺ and Co³⁺ valence states, respectively, which were very close to the values we obtained¹⁹. Since the average cobalt valence is 3^+ , the presence of the Co²⁺ satellite implies also the presence of Co⁴⁺, whose satellite cannot be observed¹⁹.



Figure S7 (a) The C 1*s* spectra of a 100 nm thick BM-SCO before etching and the Co 2*p* core level spectra with the energy position calibrated respect to C 1s (b) The Co 2*p* core level spectra (circles symbols) together with the fit results (continuous black lines) measured during the XPS depth profile on the BM-SCO sample with same thickness and grown in the same conditions of the film of panel (a).

During the XPS depth profile, we also acquired the valence band spectra (VB) at different etching thickness, whose results are reported in the main manuscript.

We performed a qualitative fit of the VB region with a number of components following ref.²¹, after subtracted a Shirley background. With respect to ref. 21 the component closest to the Fermi level, namely the Co 3d band, is now splitted into A and A', as shown in Figure S8a. The main results of the fitting are summarized in the panels b and c. In panel b we report the energy distance between the O 2p and Co 3d bands (A and A'), in panel c we report the A/A' area ratio and the energy distance between the A and A' components.



Figure S8 (a) VB spectra of the 100 nm thick BM-SCO film measured by XPS depth profile after removal by etching of about 10 nm from the surface, showing the most relevant components obtained from the fitting procedure, i.e. A, A' and O 2p. (b) Behavior with the etching thickness of the energy distance between the O 2p and Co 3d bands (A and A') obtained from the fitting. (c) Behavior with the etching thickness of A/A' area ratio and energy distance between the two A and A' components obtained from the fitting.



S6: Partial Density of States (pDOS) plots of Co 3d and O 2p obtained through DFT calculations.

Figure S9: Projected Density of states (pDOS) in the BM- SCO thin films. (a) pDOS of Co 3d in BM-SCO. (b) pDOS of O 2p in BM-SCO. (c) pDOS of Co 3d in BM-SCO with oxygen vacancy. (d) PDOS of O 2p in BM-SCO with oxygen vacancy. The positive (negative) scale in the vertical axis represents the spin-up (spin-down) components, respectively. The pDOS of BM-SCO with no strain and 4% biaxial compressed strain are shown with dark (blue) and light (orange) lines, respectively.

S7: Performance test of water splitting electrolyzer with SCO thin film anode

The preliminary tests were carried out using the 25 nm and the 100 nm BM-SCO films grown on LAO in a two-electrode system (cathode and anode) for water electrolysis reactions. The two-electrode electrolyzer setup only consisted of the BM-SCO thin film anode and the Pt cathode in 1.0 M KOH solution, which was the same of the real water splitting devices. In Figure S10a, the gas bubble produced on the surface of the two electrodes during reaction can be clearly observed demonstrating that the water splitting reaction happened. In Figure S10b and c the current-potential profiles is shown, obtained from the two-electrode electrolyzer containing the BM-SCO anode with two different thickness, and the time dependent potential response of the two samples in long time water-splitting reaction at a constant current density of 5 mA/cm². For the 100 nm sample, the water splitting onset potential was approximately 1.50 V and the current density of about 4.6 mA/cm² was obtained at 2V potential difference between anode and cathode. For the 25 nm BM-SCO film anode, both onset potential and driving potential for achieving the same current density increased. Unfortunately, the watersplitting cell performances deteriorated for both BM-SCO thin film anodes. However, the chronoamperometric test at 5 mA/cm² for an one-hour water-splitting reaction demonstrated a better performance stability for the 25 nm sample. Further investigation to clarify this aspect will be performed.



Figure S10: (a)Two-electrode electrolyzer with SCO thin film anode for water splitting during experiment. (b) Current-potential profiles from the two-electrode electrolyzer during water splitting reaction (c) Time dependent potential response during 1-hour chronoamperometric water-splitting reaction using the two-electrode electrolyzer (SCO anode and Pt cathode) at a constant current density of 5 mA/cm².

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