

Supplementary Information

Direct Evidence of Cobalt Oxyhydroxide Formation on a $\text{La}_{0.2}\text{Sr}_{0.8}\text{CoO}_3$ Perovskite Water Splitting Catalyst

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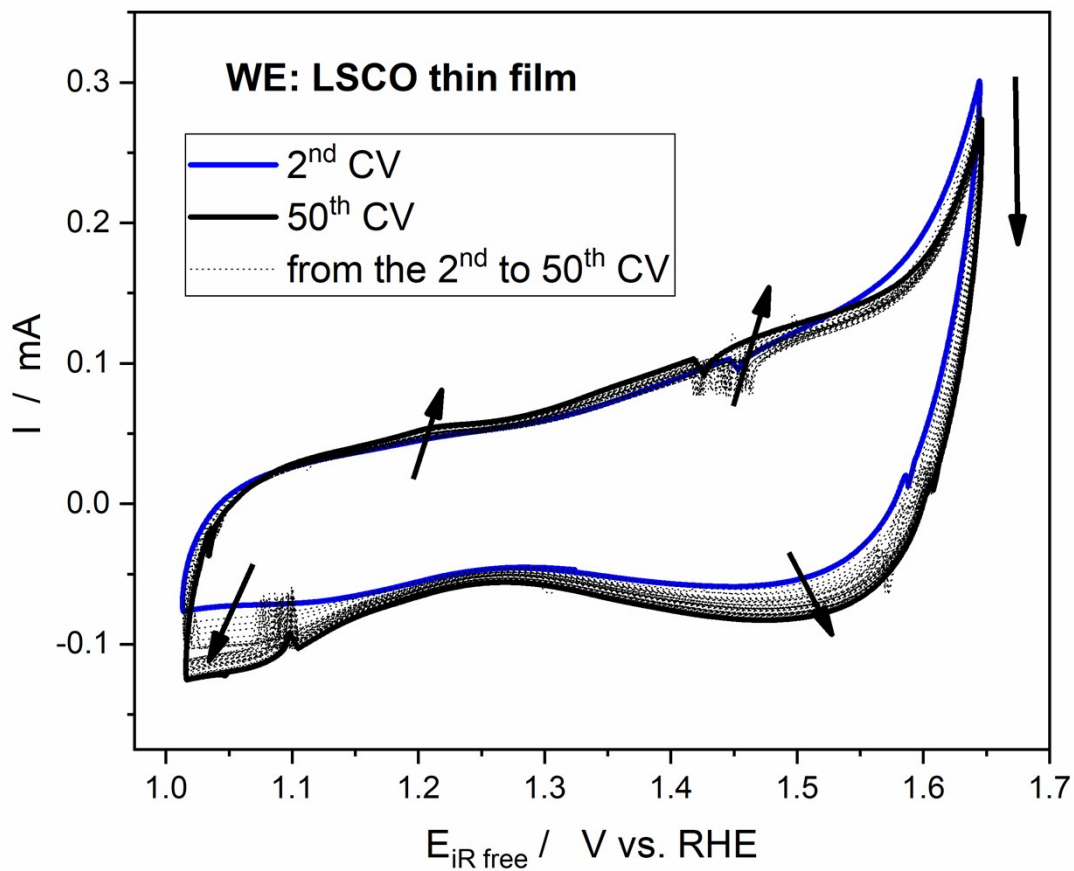


Figure S1: iR corrected CVs of the LSCO sample acquired between 1 and 1.65 V vs RHE (the second and the 50th Cvs are shown with ticker blue and black lines, respectively).

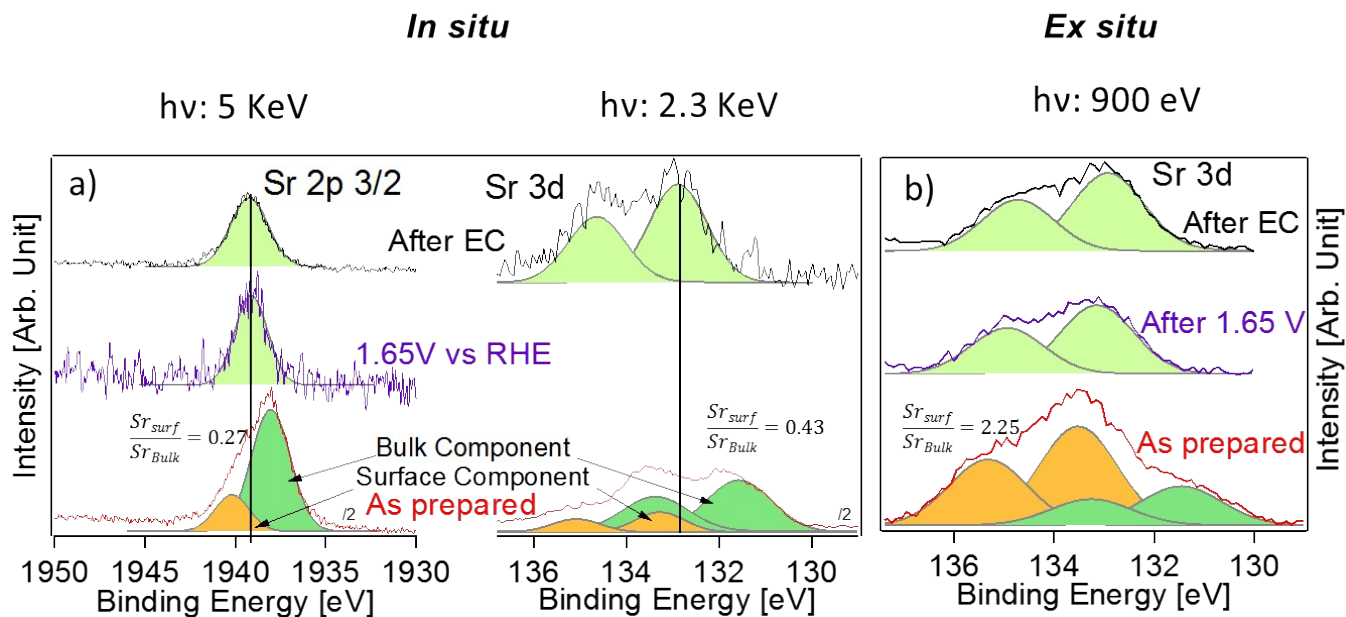


Figure S2: Deconvolution of Sr 3d and Sr 2p XPS spectrum taken at 2300 eV and 5000 eV, respectively, in the case of the *in situ* experiment; (a) Sr 3d acquired at $h\nu = 900 \text{ eV}$ in the case of the *ex situ* experiment; (b) Red, purple and black curve corresponds to the “As prepared”, “Under 1.65V vs RHE”/“After 1.65V vs RHE) and “After electrochemistry” state, respectively. The dark green component corresponds to the Sr bulk signal coming from the perovskite, the orange corresponds to segregated strontium, and the light green corresponds to amorphous strontium obtained after electrochemistry.

<i>Ex situ</i> (KE= 780 eV)						
	As Prepared		After 1.65 V vs RHE		After EC	
	BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)
Sr _{bulk} 3d _{5/2}	131.5±0.2	1.9	133.1±0.15	1.7	132.9±0.15	1.6
Sr _{surf} 3d _{5/2}	133.6±0.2	1.8	X	X	X	X
O _{bulk} 1s	528.9±0.25	3.0	529±0.3	2.7	529.0±0.3	2.6
O _{surf} 1s	531.7±0.25	2.9	531.6±0.3	2.8	X	X
O _{Hydroxyl} 1s	X	X	530.6±0.3	2.8	530.6±0.3	3.0

<i>Ex situ</i> (KE= 480 eV)						
	As Prepared		After 1.65 V vs RHE		After EC	
	BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)
Sr _{bulk} 3d _{5/2}	131.4±0.25	1.9	133.1±0.15	1.3	133.0±0.1	1.3
Sr _{surf} 3d _{5/2}	133.3±0.25	1.5	X	X	X	X
O _{bulk} 1s	528.9±0.15	2.3	529.0±0.2	2.4	529.0±0.25	1.9
O _{surf} 1s	531.5±0.15	2.3	531.8±0.2	2.4	531.6±0.25	2.2
O _{Hydroxyl} 1s	X	X	530.8±0.2	2.6	530.6±0.25	2.3

Table S1: XPS core level peak fitting parameters for the *ex situ* experiment. All peaks were fitted using Gaussian line shape and Shirley background line shapes. For Sr 3d_{5/2} a branching ratio of 1.5 and a spin-orbit split of 1.8 eV was fixed with respect to the Sr 3d_{3/2} peak. All areas are corrected for photon flux and cross section. X represents a missing data point due to the peak not being present/detectable.

<i>In situ</i> (h ν =2300 eV)						
	As Prepared		Under 1.65 V vs RHE		After EC	
	BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)
Sr _{bulk} 3d _{5/2}	131.6±0.15	1.7	X	X	132.9±0.2	1.6
Sr _{surf} 3d _{5/2}	133.3±0.15	1.2	X	X	X	X
O _{bulk} 1s	528.8±0.15	1.6	X	X	529.0±0.3	1.4
O _{surf} 1s	531.5±0.15	2.1	X	X	531.6±0.3	1.9
O _{Hydroxyl} 1s	X	X	X	X	530.6±0.3	1.3

<i>In situ</i> (h ν =5000 eV)						
	As Prepared		Under 1.65 V vs RHE		After EC	
	BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)
Sr _{bulk} 2p _{3/2}	1938.0±0.15	2.4	1938.8±0.15	2.1	X	X
Sr _{surf} 2p _{3/2}	1940.2±0.15	2.2	X	X	X	X
O _{bulk} 1s	528.9±0.25	1.7	529.0±0.35	1.6	X	X
O _{surf} 1s	531.5±0.25	2.3	531.6±0.35	2	X	X
O _{Hydroxyl} 1s	X	X	530.6±0.35	1.4	X	X

Table S2: XPS core level peak fitting parameters for the *in situ* experiment. All peaks were fitted using Gaussian line shape and Shirley background line shapes. For Sr 3d_{5/2}, a branching ratio of 1.5 and a spin-orbit split of 1.8 eV were fixed with respect to the Sr 3d_{3/2} peak. For the Sr 2p core level peak, due to the spin-orbit splitting of 67 eV, only the Sr 2p_{3/2} was acquired. X represents a missing data point due to the peak not being present/detectable or spectra not being acquired.

<i>Ex situ</i>		
Condition	KE (eV)	Sr/Co ratio
As prepared	780	3.54±0.14
After 1.65V vs RHE	780	1.06±0.1
After EC	780	0.77±0.09
<i>In situ</i>		
Condition	hν (eV)	Sr/Co ratio
As prepared	2300 eV	3.95±0.15
	5000 eV	0.69±0.08
Under 1.65V vs RHE	5000 eV	0.24±0.06
After EC	2300 eV	0.75±0.08

Table S3: Evolution of Sr/Co ratio for both *in situ* and *ex situ* experiment

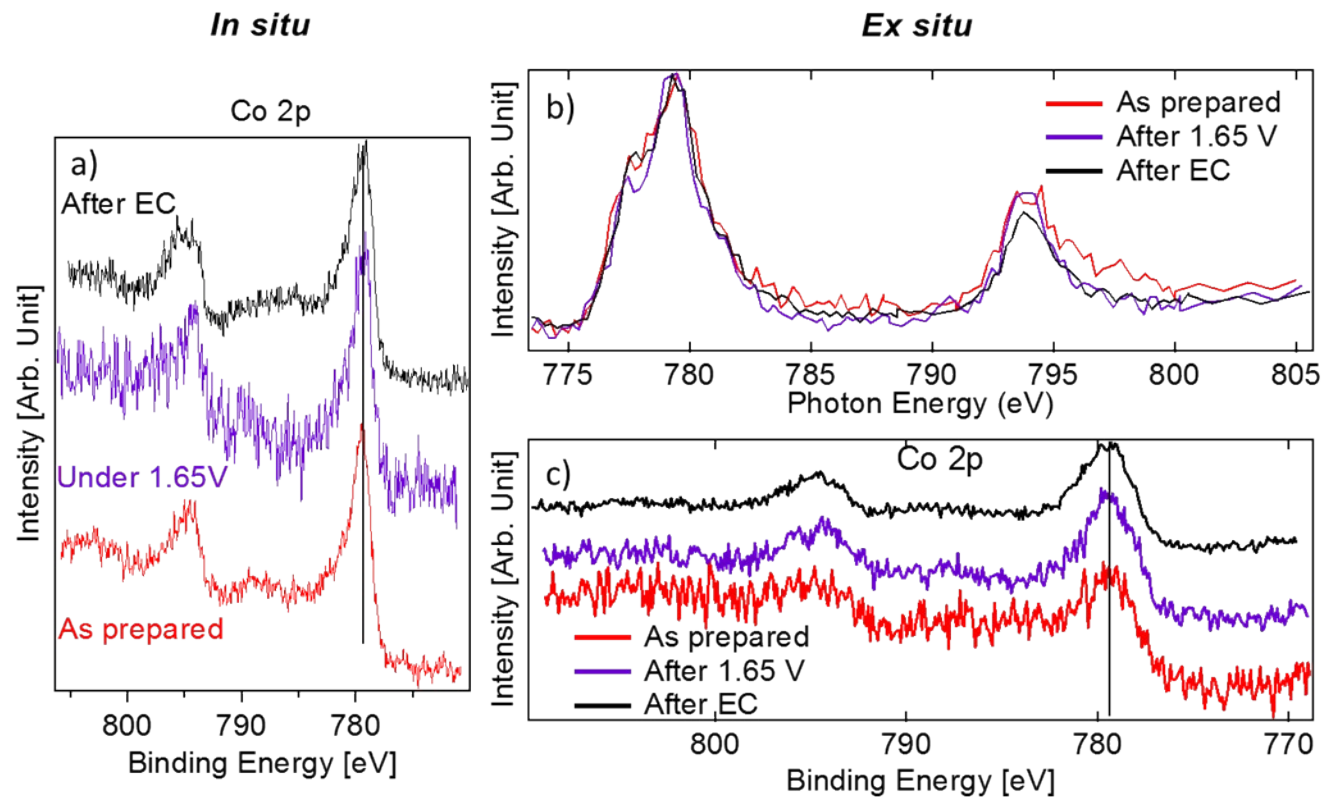


Figure S3: XPS spectra of the Co 2p core level peak acquired during the *in situ* experiment (a) and *ex situ* experiment (c) as well as Co L edge NEXAFS (b) acquired during the *ex situ* experiment. Red, purple and black curves correspond to the “as prepared”, the “After 1.65V vs RHE” and the “After electrochemistry” state, respectively. For the *in situ* experiment, the “as prepared” state was acquired with $h\nu = 2300$ eV, the “under 1.65V vs RHE” with $h\nu = 5000$ eV and the “After electrochemistry” with $h\nu = 2300$ eV. For the *ex situ* experiment, all Co 2p have been acquired with $h\nu = 1280$ eV.

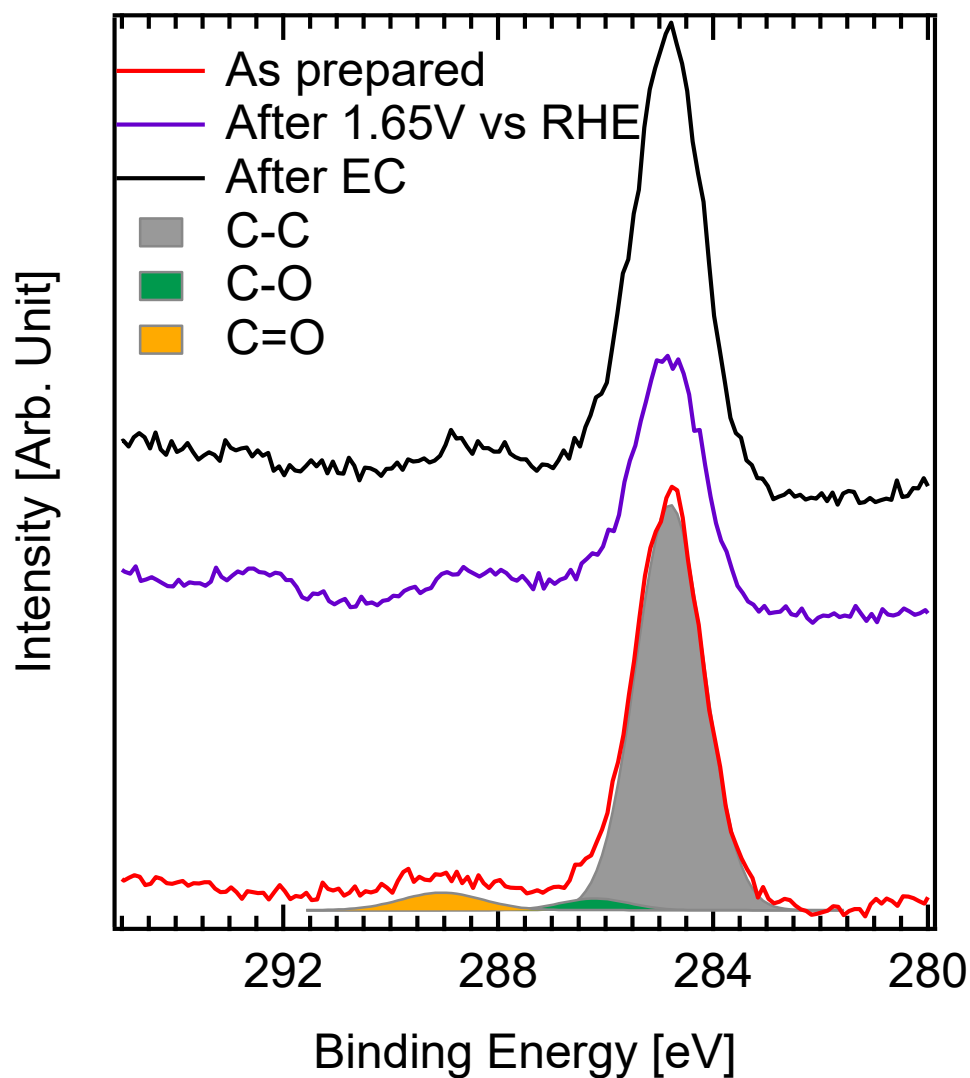


Figure S4: Photoemission spectra of the C 1s core level peak acquired with $h\nu = 810$ eV during the *ex situ* experiment. Red, purple and black curves correspond to the “as prepared”, the “After 1.65V vs RHE” and the “After electrochemistry” state, respectively. Concerning deconvolution, grey color corresponds to the C-C (aliphatic) component, green to C-O component and orange to C=O (carbonate) components.

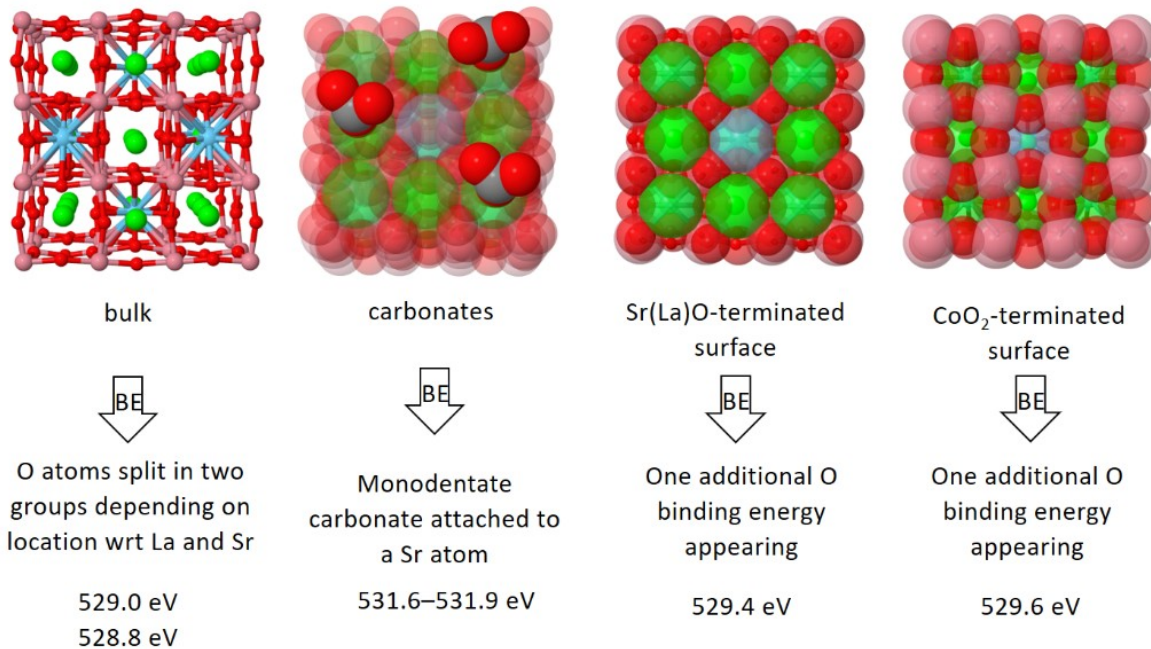


Figure S5: Geometrical configurations and corresponding O 1s binding energies for the bulk perovskite, Sr/La terminated and CoO₂ terminated surfaces of perovskites, as well as surface carbonate species simulated on the (001) surface termination.

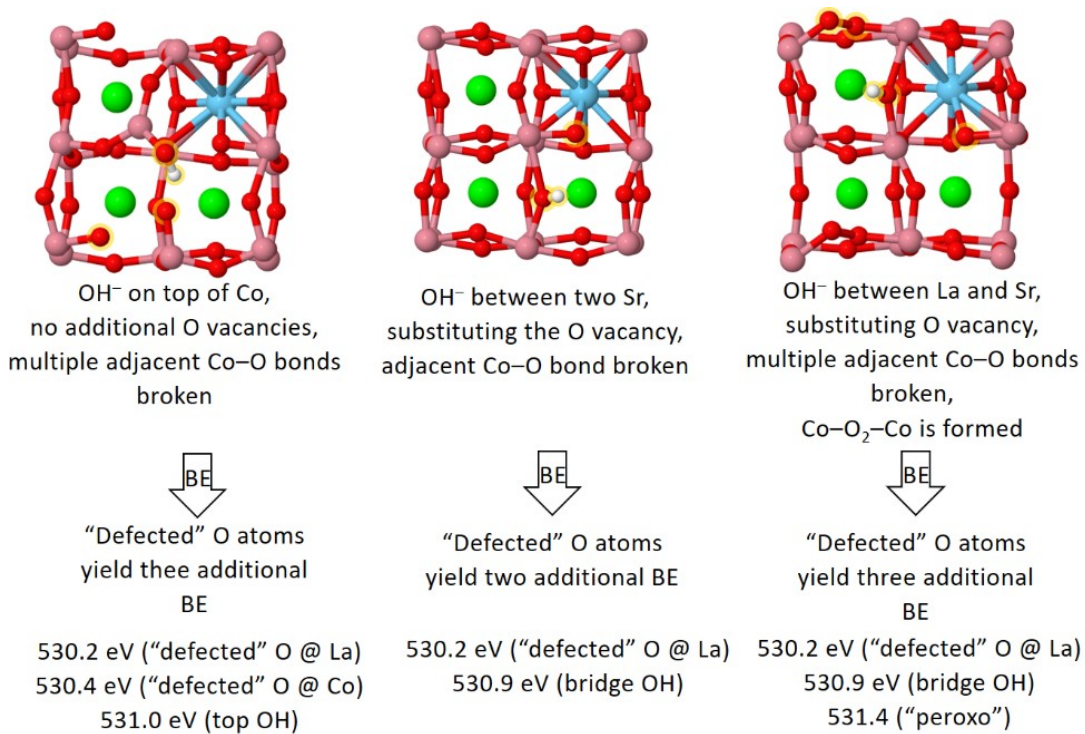


Figure S6: Geometrical configurations and corresponding O 1s binding energies for some of the possible surface hydroxyl species systems considered in this study, including the structures

corresponding to the adsorption of OH⁻ groups on the surface and substitution of a surface oxygen defect with an OH⁻ group simulated on the (001) surface termination.

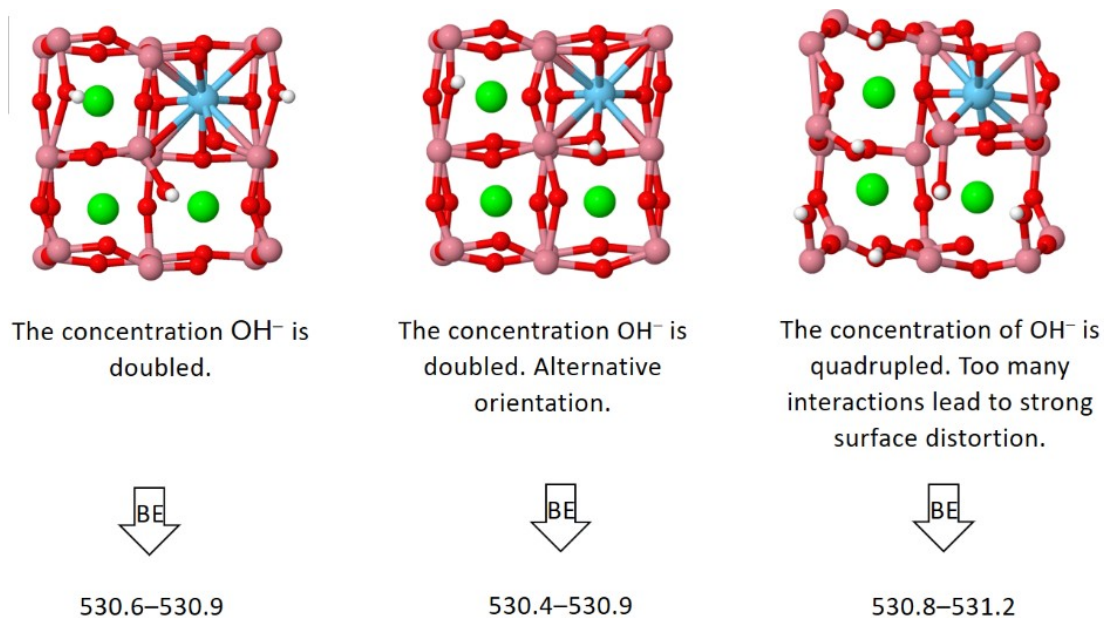


Figure S7: Geometrical configurations and corresponding O 1s binding energies for some of the possible surface hydroxyl species systems considered in this study simulated on the (001) surface termination. Here, the concentration of the OH⁻ groups increased compared to Figure S5.

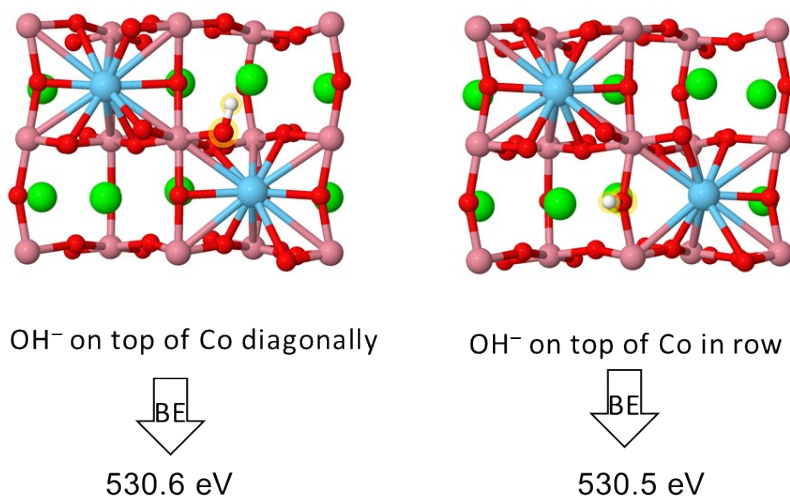


Figure S8: Geometrical configurations and corresponding O 1s binding energies for some of the possible surface hydroxyl species systems considered in this study using a (110) surface termination.

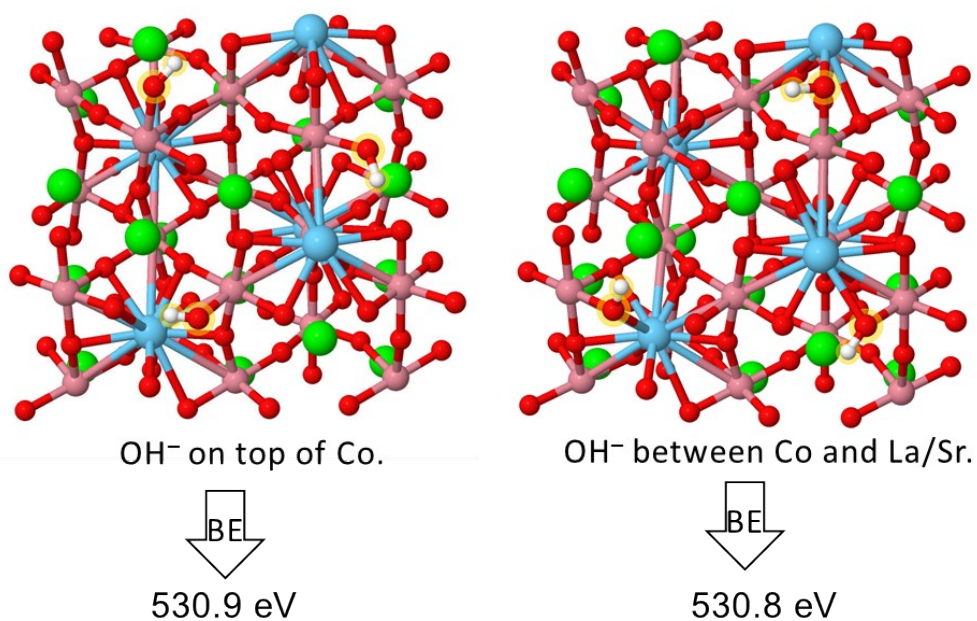


Figure S9: Geometrical configurations and corresponding O 1s binding energies for some of the possible surface hydroxyl species systems considered in this study using a (111) surface termination.

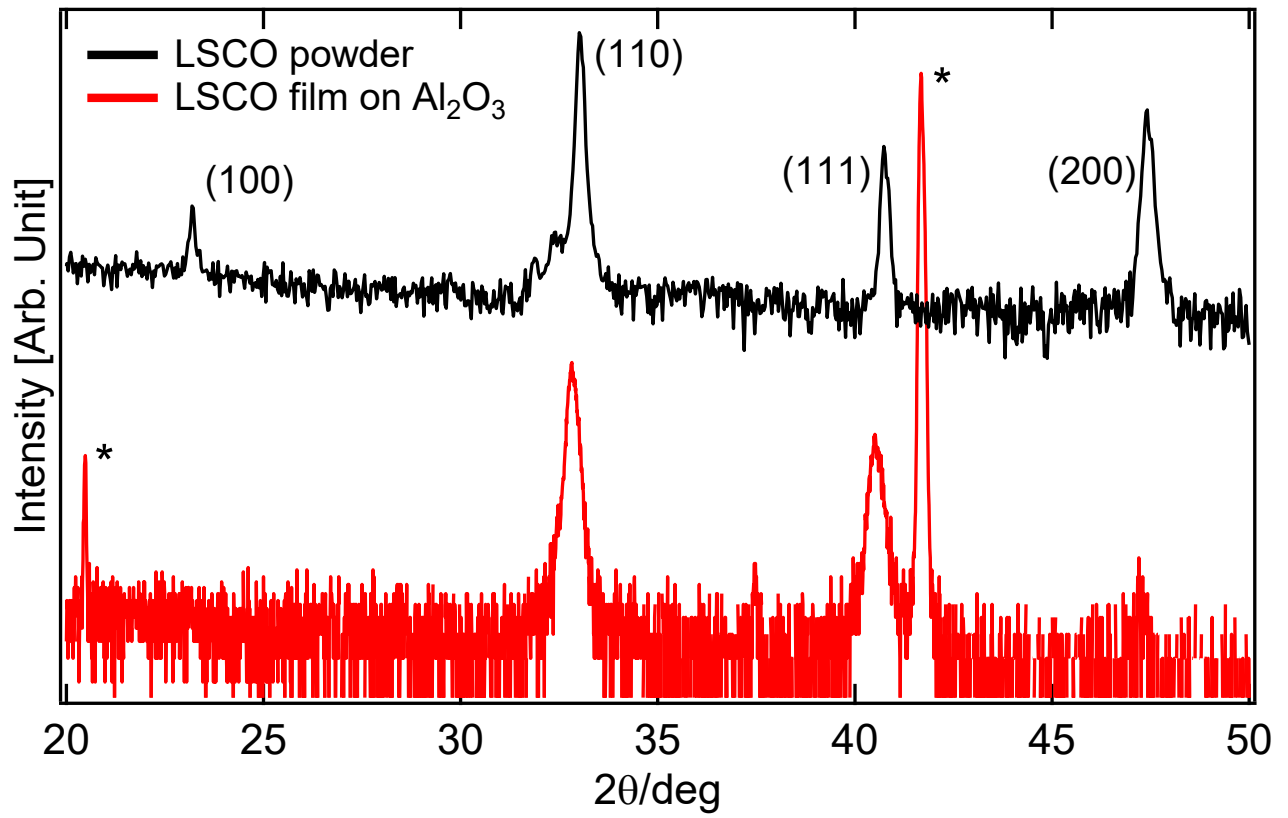


Figure S10: XRD plot of a LSCO films (red) compared with that of powders (black). The symbol * indicates the diffraction peaks of the Al₂O₃ substrate.

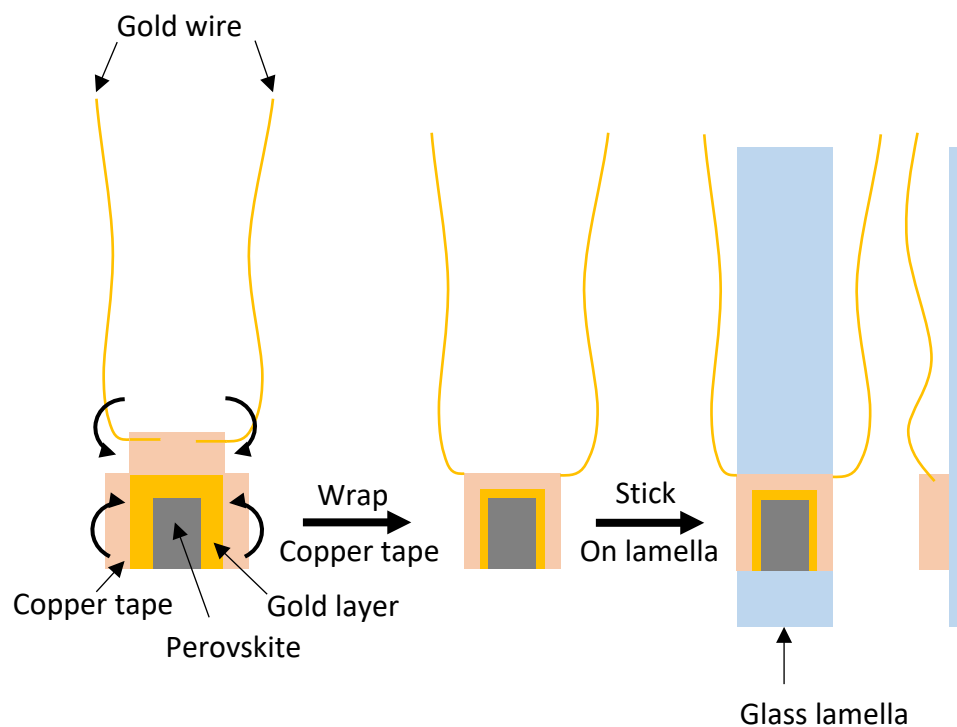


Figure S11: Schematics of the perovskite electrode used for both *ex situ* and *in situ* experiments, where a gold frame ensured the connection to the three electrode setup. The copper tape was first wrapped around gold wires, leaving enough length to cover the top gold layer. The side copper tape was then folded on the side gold layer.