Supplementary information

Low Energy Ion Scattering (LEIS) experiments:

The LEIS experiments of the single crystals were performed in a Qtac100 instrument (ION-TOF GmbH, Tascon GmbH, Münster). Each surface was measured using two different noble gas ions: He^+/3 keV and $^{22}Ne^+$/5 keV. It should be noticed that the Ne used was the isotope ^{22}Ne (and not ^{20}Ne) and therefore the peak positions in the spectra are found at lower energies than normally expected for ^{20}Ne. The reference high-purity NiO (Alfa Aesar, 99.998%), SrO (Sigma Aldrich, 99.9%) and La_2O_3 (Alfa Aesar, 99.9%) were polycrystalline very fine powders, they were pressed to form a microscopically flat surface and measured using He^+/3 keV and $^{20}Ne^+$/5 keV noble gas ions in a Qtac100 instrument (ION-TOF GmbH, Imperial College London). Previous to the measurement, the SrO and La_2O_3 were annealed at 850 and 1000 ºC, taken out of the furnace at high temperature, rapidly quenched and pressed as a pellet to avoid water uptake and carbonate formation. They were pressed into tablets, brought into the vacuum and treated with atomic oxygen until all organic contamination was removed from the surface.

In addition, to estimate the sensitivity and detection limit of Ni for the ^{22}Ne isotope, the neutralization rate was determined by using the characteristic velocity method based on Hagstrum's model.[1] The scattering cross-sections for Ni using ^{20}Ne and ^{22}Ne as primary ions were calculated using the Moliere approximation to the Thomas-Fermi potential (TFM). By measuring the Ni peak of the reference NiO powder for six different initial energies (from 4 to 7 keV) using $^{20}Ne^+$, the characteristic velocity V_c (a measure of the characteristic neutralization probability) was found to be 1.17×10^5 m/s, and the ion fractions of the backscattered ions (P^+) have been calculated to be 0.21 and 0.18 for ^{20}Ne and ^{22}Ne, respectively. Finally, the elemental sensitivity factors (η) have been calculated as the product of the ion fraction P^+ times the differential scattering cross-section ($d\sigma/d\Omega$). As a result the sensitivity for Ne^{22} has been calculated to be 80% of that for Ne^{20}, and the detection limit of Ni has been calculated to be 10% of the surface fraction.

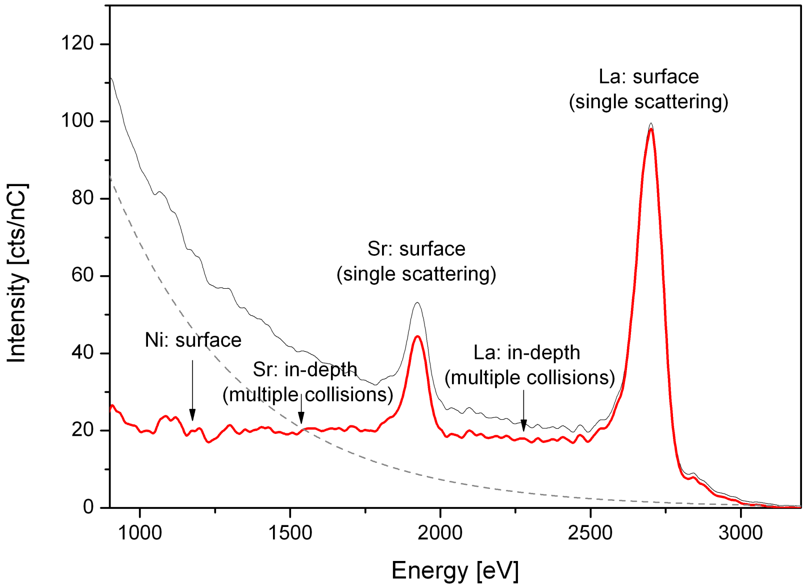

Figure S1. ^{22}Ne LEIS energy spectrum obtained for the (110) face of the $La_{1.67}Sr_{0.33}NiO_{4+\delta}$ single crystal after heat treatment. Original data (grey line), background (dashed line) and obtained corrected spectrum (red line).

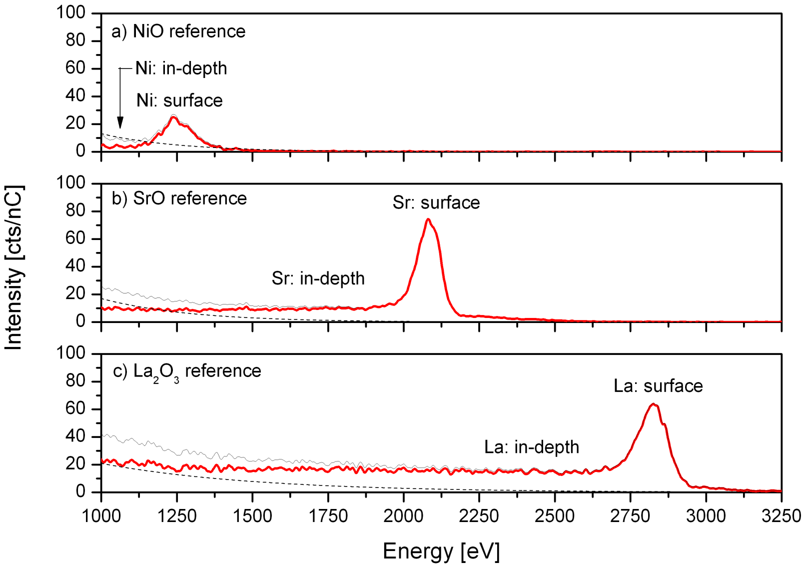

Figure S2. ^{20}Ne LEIS energy spectra obtained for the a) NiO, b) SrO and c) La_2O_3 powder references. Original data (black solid line), background (dashed black line) and obtained corrected spectrum (red solid line).

Crystal truncation rod (CTR) experiments:

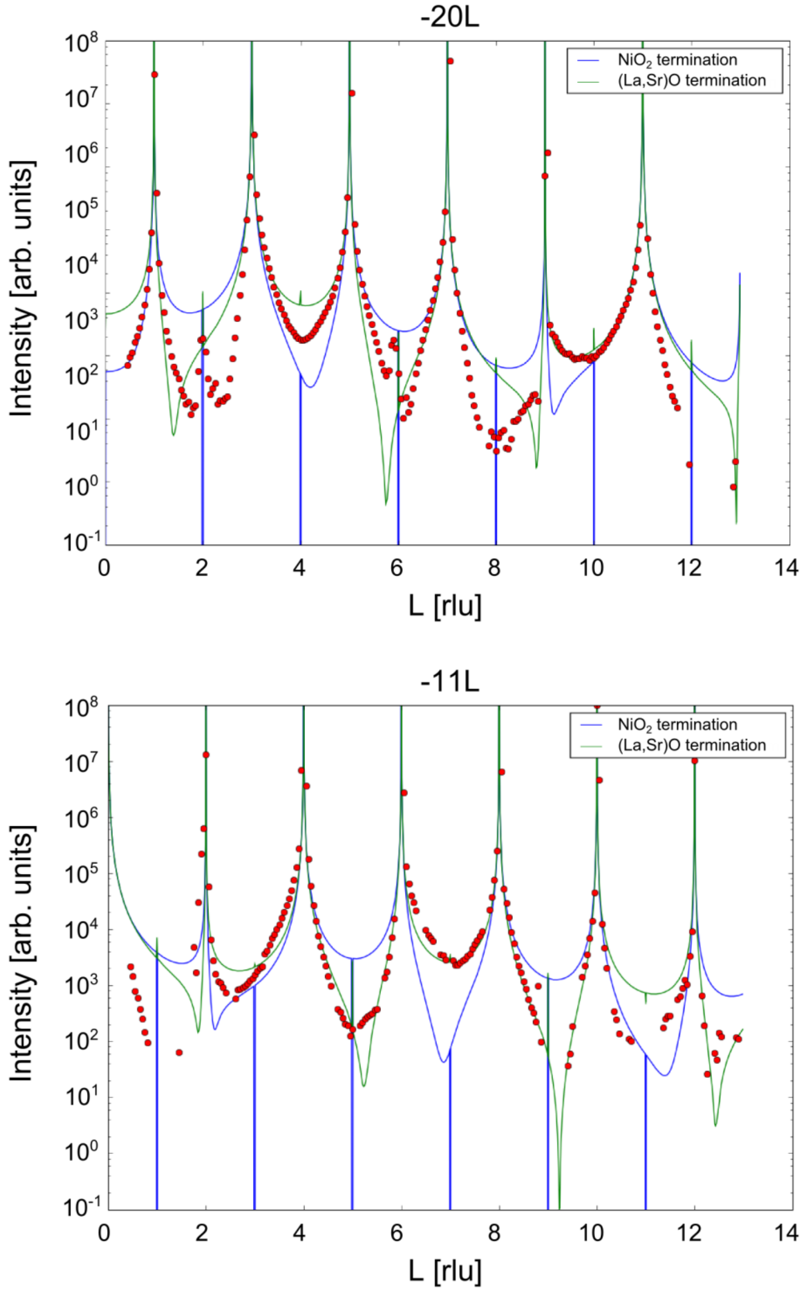

Figure S3 . Crystal truncation rods along the a) -20L and b) -11L directions in air at 450 ºC. Red dots indicate the raw data and the lines the model CTR patterns for NiO (blue) or LaO (green) termination.

Angle -resolved X-ray photoelectron spectroscopy (AR-XPS) experiments:

XPS measurements were recorded in the SPECS Surface Analysis System at CIC energiGUNE (Miñano, Spain). Monochromatic Al-K_α (1486.61 eV) radiation was used as excitation source and photoelectrons were collected with a Phoibos 150 analyser equipped with a delay-line detector. The overall depths for each photoelectron peak corresponding to the different take-off angles have been calculated based on the electron IMFP determined by the Tanuma, Powell and Penn equation[2]. The sample manipulator is fitted with high precision stepper motors so five-axis are precisely controlled through an electronic system; this allows a fine control over the photoelectrons take-off angle. Data were collected at room temperature and the base pressure in the analysis chamber was 10^{-9} mbar. The crystals were mounted in molybdenum sample holders using adhesive carbon tape to ensure a good electrical conductivity.

X-ray photoelectron spectroscopy spectra from lanthanide materials in the binding energy range from 0-1250 eV, besides the spin-orbit splitting, exhibit a very complex structure due to final state effects. This fine electronic structure of lanthanide compounds has been studied in the past.[3] Moreover, in the Sr doped La_2NiO_4 crystals, the Ni $3p_{3/2}$ and the La $3d_{3/2}$ peaks are overlapped, therefore, it is impossible to exactly determine the Ni^{3+} and the Ni^{2+} concentrations by XPS. Previous works have reported methods to separate the Ni $3p_{3/2}$ and the La $3d_{3/2}$ peaks in XPS spectra.[4] However, these methods cannot provide information about the separation of the different valence states of Ni.

Figure S4 shows the La $3d_{5/2}$, Ni $2p_{3/2}$, and La $3d_{3/2}$ peaks as a function of the photoelectron take-off angle corresponding to overall depths of 0.5, 2 and 4 nm from the as-cleaved and annealed (72 hours in air at 450 ºC) crystals.[2] The standard energy positions [5] for Ni^{3+} and Ni^{2+} are marked with dotted lines. Since the lines are strongly overlapped with the La $3d_{3/2}$ shake-up peak, from these spectra it is not possible to determine the Ni^{3+}/Ni^{2+} ratio precisely. The experimental data are plotted against an envelope line of the La $3d_{5/2}$and La $3d_{3/2}$ peaks along with their corresponding shake-up features. The differences between this envelope and the experimental data account for plasmon loss peaks and Ni $2p$ peaks. It can be deduced in both samples that a mixture of Ni^{3+} and Ni^{2+} is present and the amount of Ni decreases as the surface is approached, in good agreement with LEIS and CTR results. Additionally, in the as-cleaved sample, the amount of Ni^{3+} is greater than in the annealed, especially when comparing the 4 nm regions

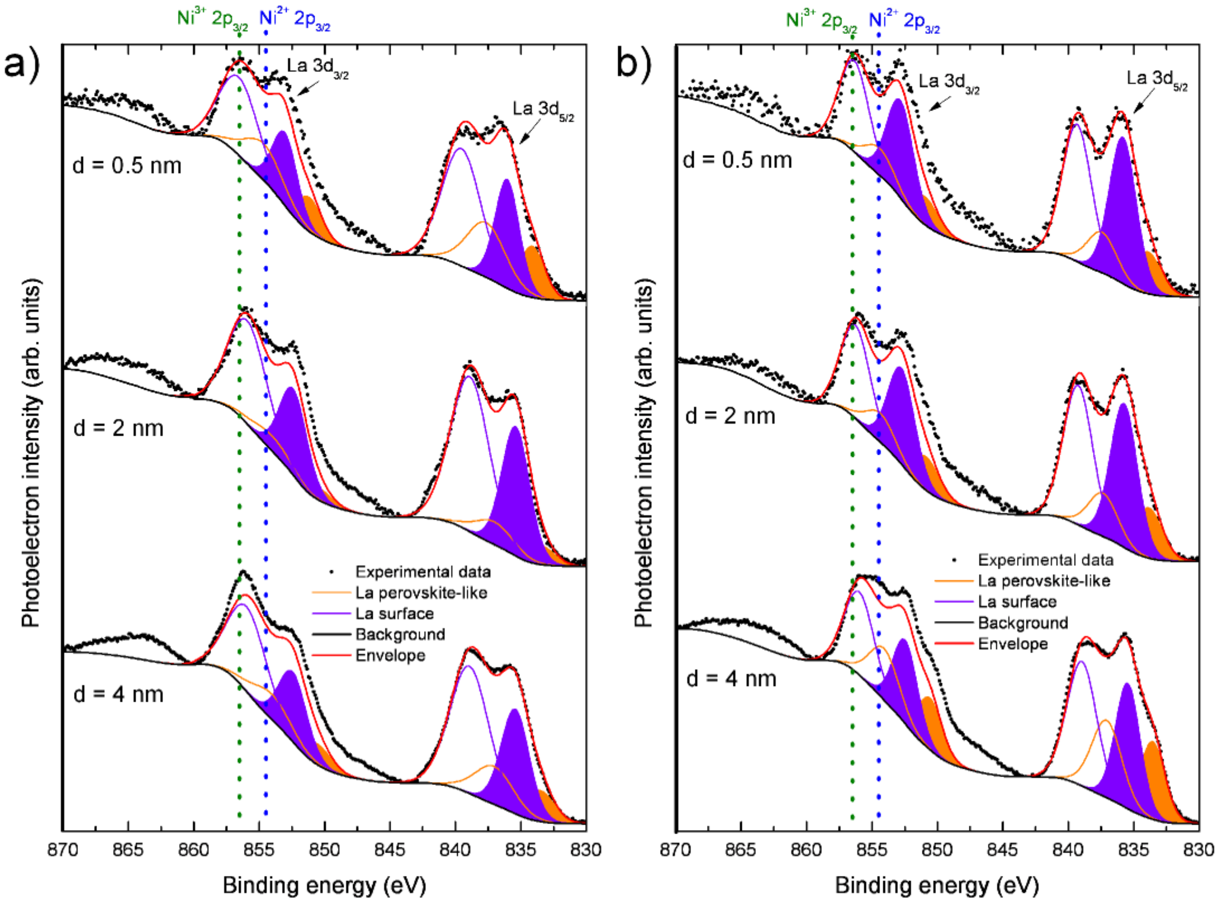

Figure S4. Angle-resolved XPS spectra of the La 3*d* and Ni 2*p* core levels for the (001) face of the $La_{1.67}Sr_{0.33}NiO_{4+\delta}$ single crystal a) before and b) after the heat treatment. Each spectra has been recorded at a different photoelectron take-off angle, therefore the information corresponds to three different surface regions: 0.5, 2 and 4 nm. In orange the contribution from perovskite-like La and in violet the component corresponding to La surface species (e.g. $La(OH)_3$ and La_2O_3). The full peaks correspond to the main photoelectron peak; the solid lines represent the final-state effects (shake-up). The convolution of the La 3*d* core level lines is the red line where no contribution from plasmon losses (at 847 and 865 eV) or Ni 2*p* core levels (marked in blue for Ni^{2+} and green for Ni^{3+}) has been taken into account.

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3. D. J. Lam, B. W. Veal and D. E. Ellis, *Physical Review B*, 1980, **22**, 5730-5739.
4. S. Mickevicius, S. Grebinskij, V. Bondarenka, B. Vengalis, K. Sliuziene, B. A. Orlowski, V. Osinniy and W. Drube, *Journal of Alloys and Compounds*, 2006, **423**, 107-111.
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