

## Electronic Supplementary Information (ESI)

### Investigation of the metal-insulator transition in NdNiO<sub>3</sub> films by site-selective X - ray absorption spectroscopy.

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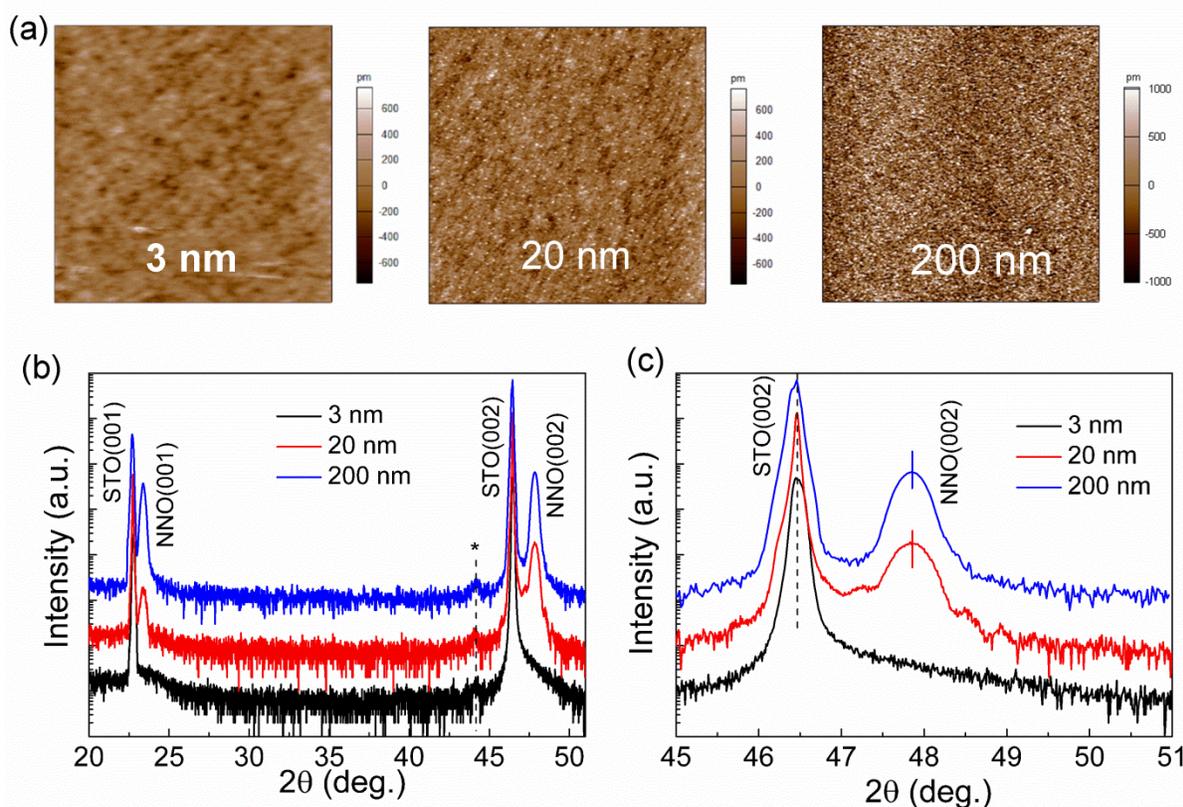
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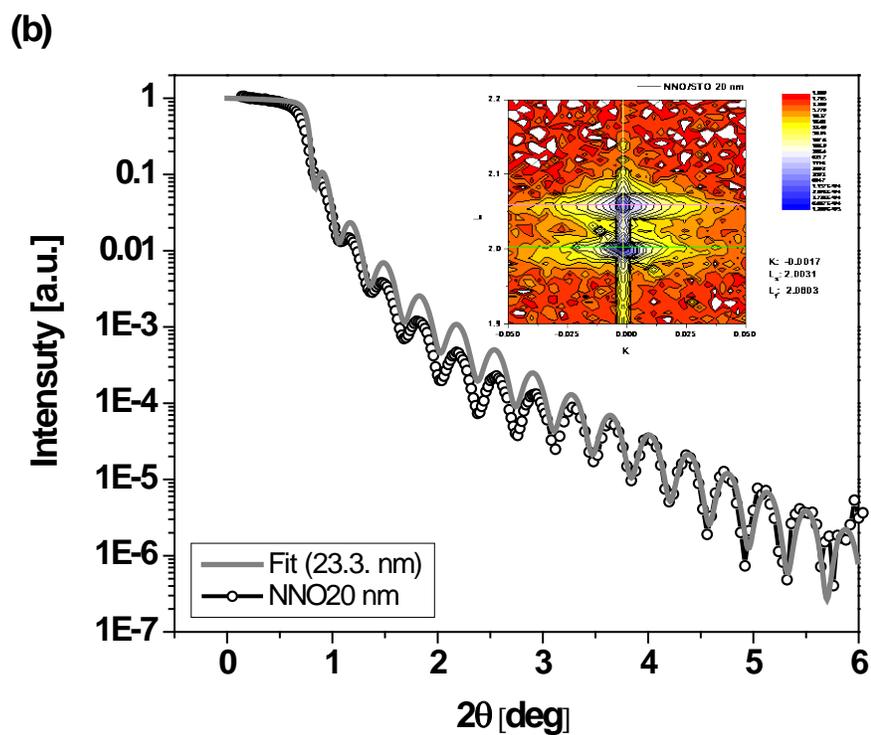
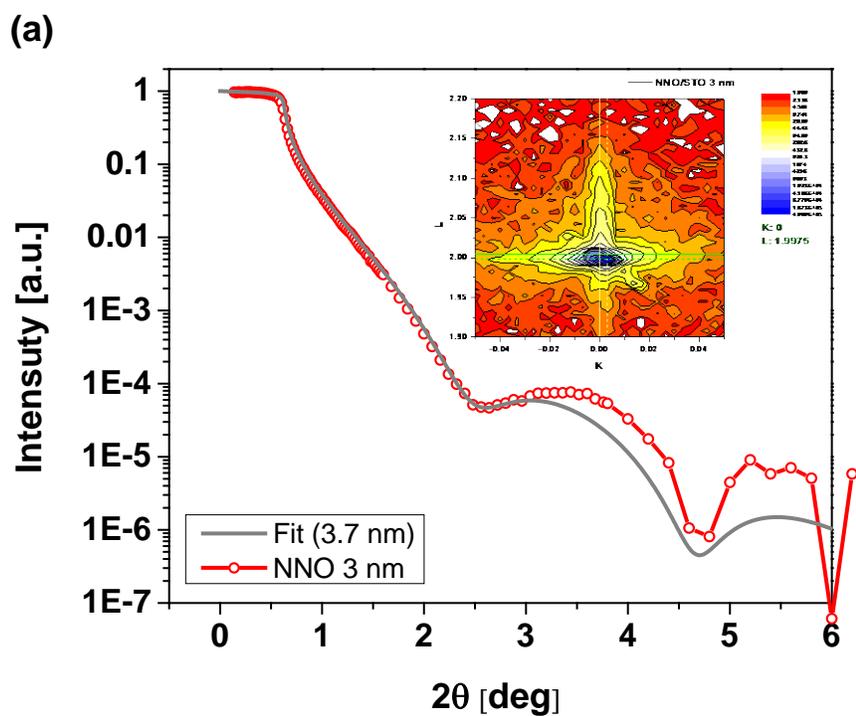
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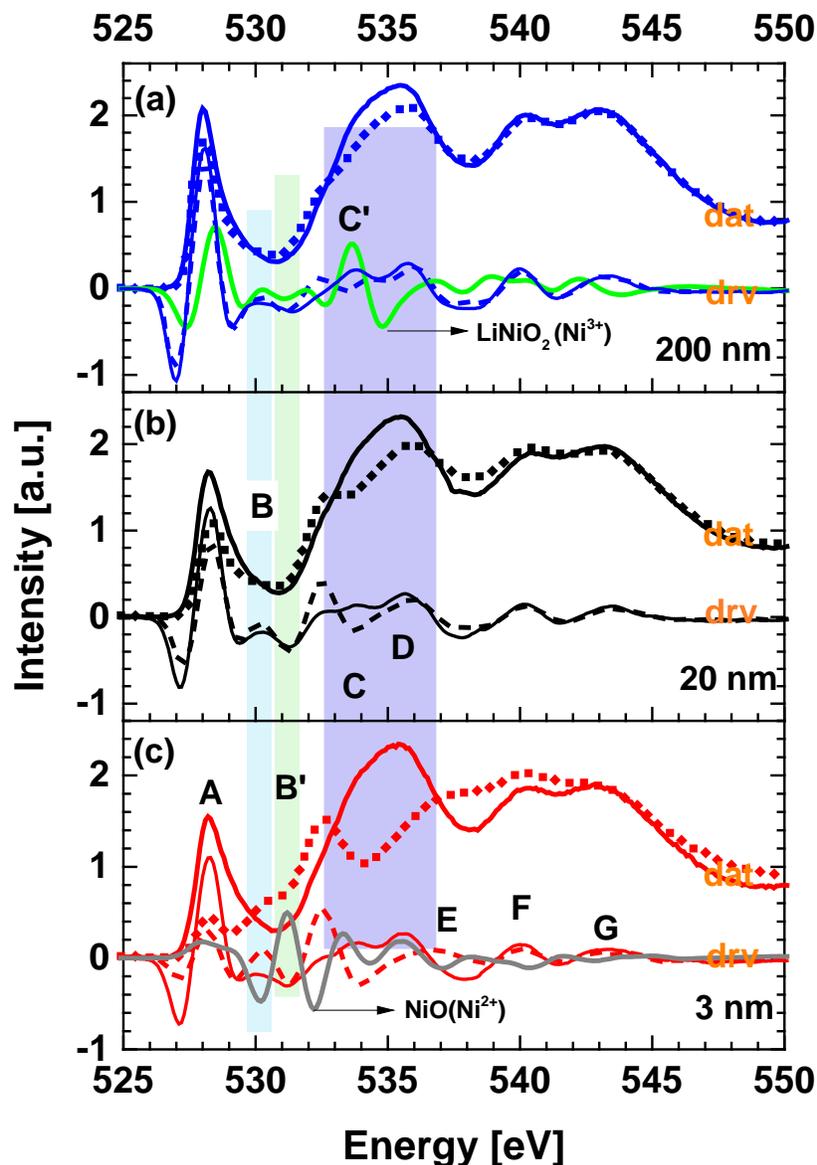
### Supporting Figures



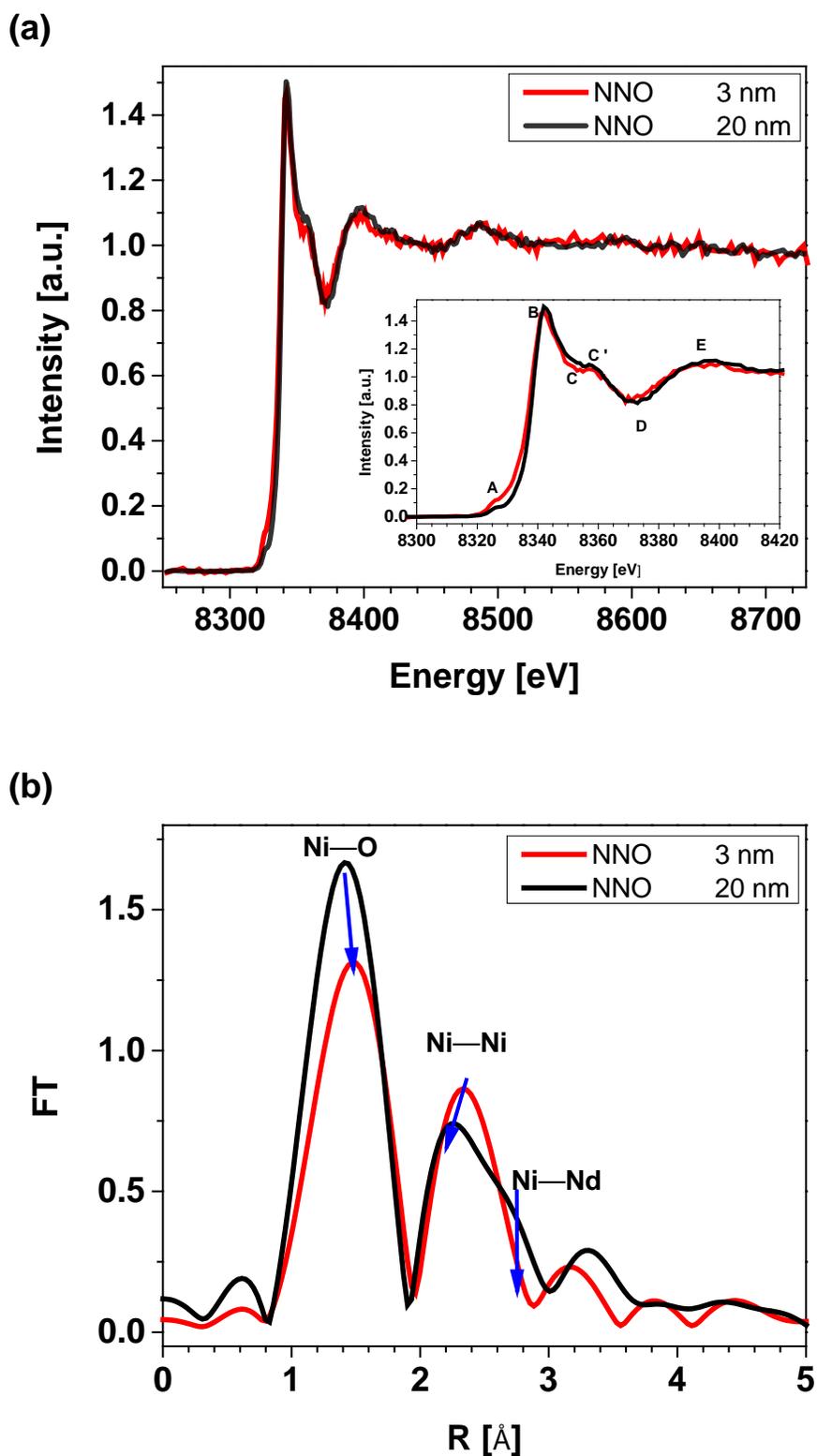
**Figure ESI 1.** (a) Topography images of NNO films with different thicknesses on STO substrates. The roughness of these samples is 113 pm, 220 pm, and 450 pm for the 3 nm, 20 nm, and 200 nm thick film, respectively. (b) XRD data of NNO films with different thicknesses. The peak of “\*” denotes the signal from Al holder in the measuring process. (c) XRD  $\theta - 2\theta$  scans around the (002) peaks. The c-axis lattice parameter is about 3.803 Å for 200 nm thick NNO film and 3.7993 Å for 20 nm thick NNO film. As the diffraction peak is difficult to distinguish from the background signal, the c-axis lattice parameter of 3-nm thick NNO film is hard to obtain.



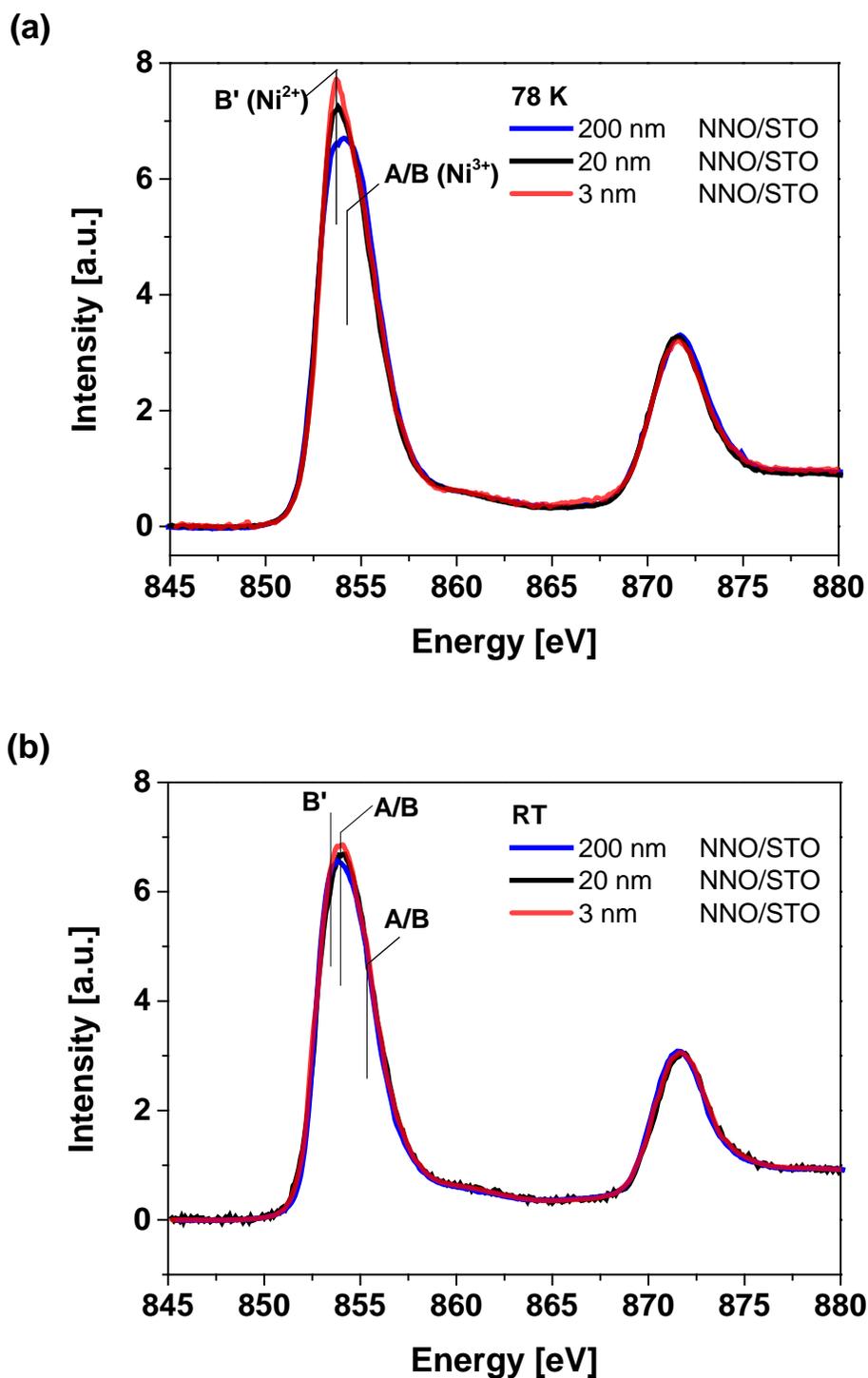
**Figure ESI 2.** Fitted (solid line) XRR data (scatters) of 3 nm and 20 nm nominally thick NNO films, (a) and (b) respectively with thickness of fit indicated in the legend. XRR fitting was performed in LEPTOS software suite. Inset shows XRD mapping.



**Figure ESI 3.** Thickness dependent comparison of O K-edge XANES (dat) and second derivative (drv) spectra acquired at room-temperature (RT) (solid line) and 78 K (dotted line) for (a) 200 nm, (b) 20 nm and (c) 3 nm NNO films. The derivative spectra for reference compounds representing  $\text{Ni}^{3+}$  and  $\text{Ni}^{2+}$  are shown in (a) and (c), respectively. XANES spectra for these references are shown in the Figure 2 of main manuscript. Most of the temperature dependent spectral weight alteration detected in the energy range related to  $\text{Ni}^{(3\pm\delta)+}$  (A (not shadowed), B) and Nd ( $5d$ ) stated (C, D) hybridized with oxygen, refer to area shadowed in light green and light purple, respectively. This observation is supporting the complex interconnection and co-dependency of covalency in  $\text{RNiO}_3$  as shown in **Figure 8** of main manuscript. Consistent with bond disproportionation as reported recently by Bisogni et. al [51].

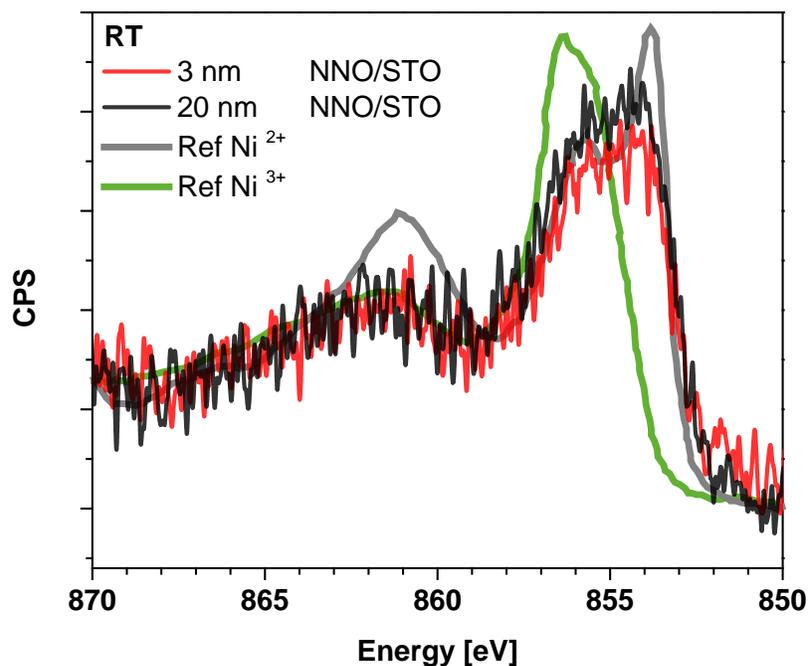


**Figure ESI 4.** (a) Ni K-edge EXAFS data for 3 nm and 20 nm NNO/STO films. The main shape-resonance in the near edge region are labeled and shown in inset. The decreased intensity of shape-resonances B, C and C' indicate decreased fraction of  $\text{Ni}^{3+}$  in 3 nm NNO/STO film. (b) Radial-distribution function for 3 nm and 20 nm NNO/STO films. For 3 nm NNO film, the shift of Ni-O peak to higher R [Å] values is consistent with bond disproportionation as reported recently by Bisogni et. al [51].

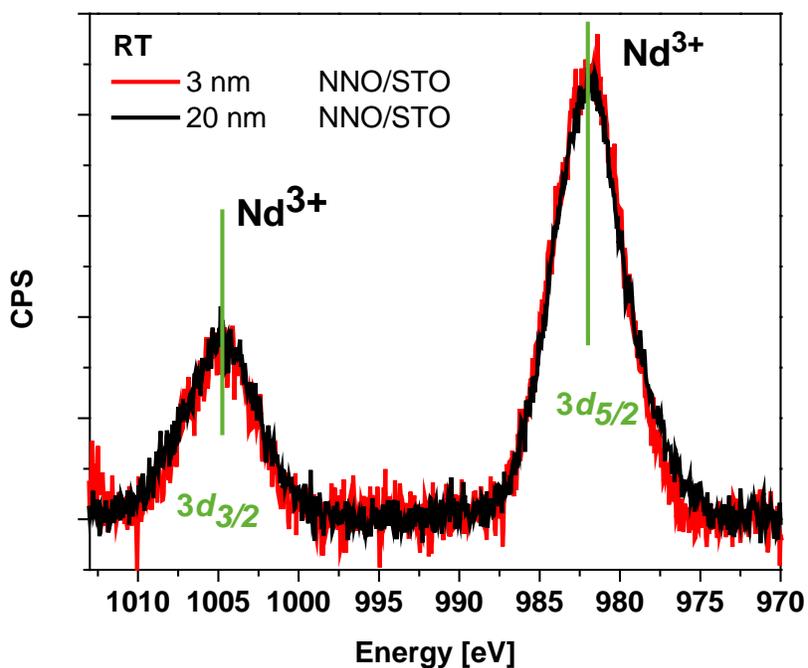


**Figure ESI 5.** Ni  $L_{32}$ -edge XANES data for 3 nm, 20 nm and 200 nm NNO/STO films acquired at temperature below MIT and RT, (a) and (b), respectively. Thickness dependent ratio of  $\text{Ni}^{2+}/\text{Ni}^{3+}$  can be traced by the intensity of peak B'. The increased fraction of  $\text{Ni}^{2+}$  is consistent with Rsheet measurements presented in the Figure 1 of main manuscript.

(a)



(b)



**Figure ESI 6.** XPS Ni  $2p_{3/2}$  and Nd 3d CL data for 3 nm and 20 nm NNO/STO films acquired at RT, (a) and (b), respectively. Presence of mixed valence state for Ni ( $\text{Ni}^{2+}$  and  $\text{Ni}^{3+}$ ) can be traced comparing recorded thickness dependent NNO data with  $\text{Ni}^{2+}$  and  $\text{Ni}^{3+}$  references, grey and green respectively. For both samples, BE of Nd 3d CL suggests that Nd accommodate valency of 3+. XPS findings are consistent with conclusion drawn from analysis of XANES spectra. Due to the insulating nature of samples at 78K, it was challenging to record XPS signal.