Supplementary information

Substrate-Surface-Structure Tuned Electrical and Magnetic Properties of $PrCoO_3/CaCoO_{2.5}$ Superlattices

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Experimental Methods

Epitaxial $[(PCO)_n/(CCO)_n]_m$ superlattices (SLs) (n = 1, 2, 5, and 10) comprising perovskite $PrCoO_3$ (PCO) and brownmillerite $CaCoO_{2.5}$ (CCO), PCO/CCO bilayer films, and $Pr_{0.5}Ca_{0.5}CoO_{3-\delta}$ (PCCO) thin films were grown on (001) STO, (001) LSAT, and (001) LAO substrates by pulsed laser deposition (PLD) with a 248 nm KrF excimer laser. Prior to the deposition of the film, the as-received substrates were annealed at 900 °C for 15 min. The thicknesses of all the samples were kept constant at ~32 nm. The optimized growth conditions for the PCO layer and the PCCO thin film were temperature of 750 °C, oxygen partial pressure of 5 Pa, laser energy density of 1 J/cm^2, and laser frequency of 3 Hz. For the CCO layer, the optimized growth conditions were temperature of 750 °C, oxygen partial pressure of 5 Pa, laser energy density of 1.3 J/cm^2, and laser frequency of 2 Hz. The target-substrate distance was fixed to 8 cm. After deposition, the films were annealed at 750 °C for 15 min at an oxygen pressure of 5 Pa before being slowly cooled to room temperature at a rate of 10 °C/min.

The crystallographic structure of the samples was examined by an X-ray diffractometer with Cu *Kα* radiation (XRD, Malvern Panalytical Empyrean). The surface microstructure was analyzed by atomic force microscopy (AFM, Cypher ES, Asylum Research). The X-ray photoelectron spectroscopy (XPS) spectra were carried out by spectrometer (ESCALAB Xi$^+$, Thermo Fisher Scientific). The electronic transport and magnetic measurements of the samples were carried out by using a physical property measurement system (PPMS, Quantum Design) and a superconducting quantum interference device (SQUID, Quantum Design) system, respectively. The magnetic field was applied to the in-plane direction of the thin films.

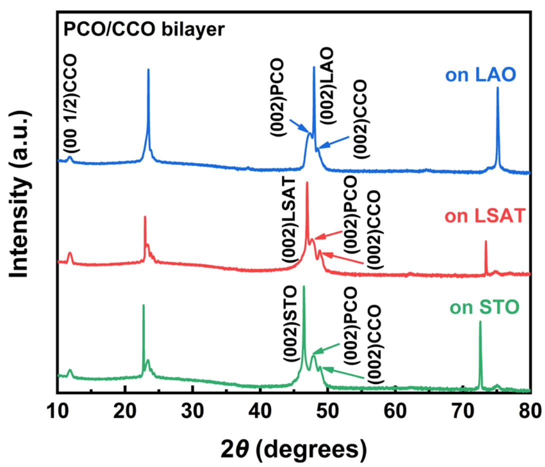

Fig. S1 X-ray diffraction *ϑ*-2*ϑ* patterns of the PCO/CCO bilayer films on various substrates.

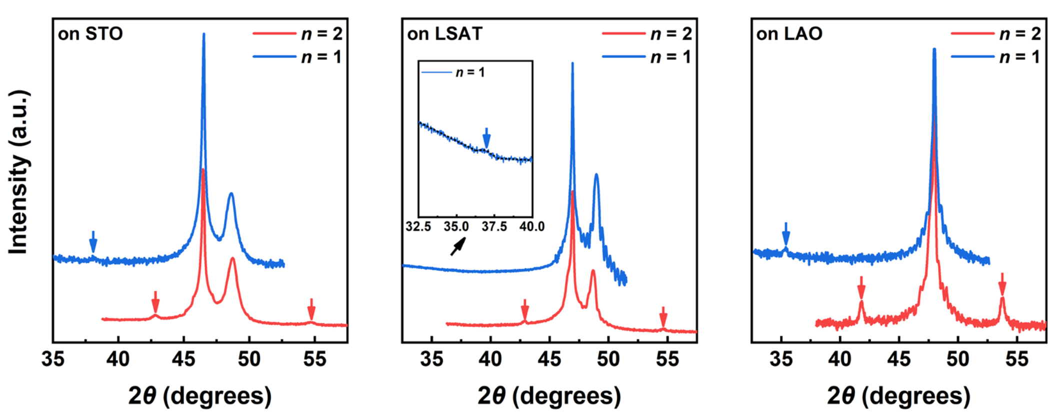

Fig. S2 Characterization of the satellite peaks for the *n* = 1 and *n* = 2 SLs.

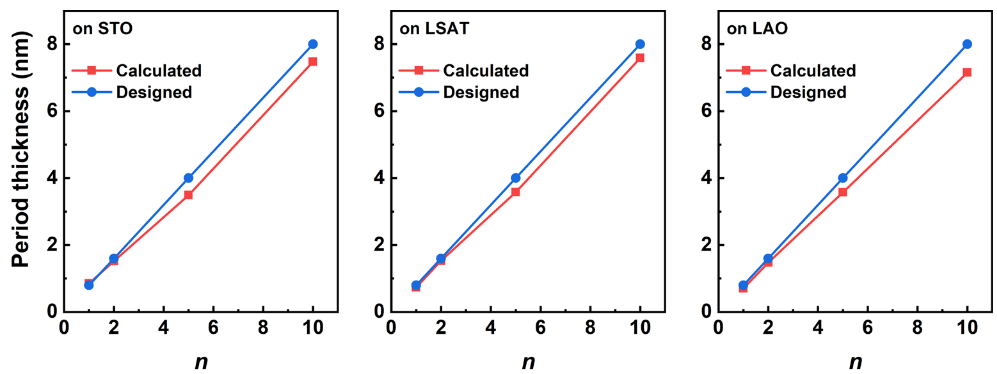

Fig. S3 Comparison of the designed period thickness with the calculated period thickness derived from the angle intervals between satellite peaks.

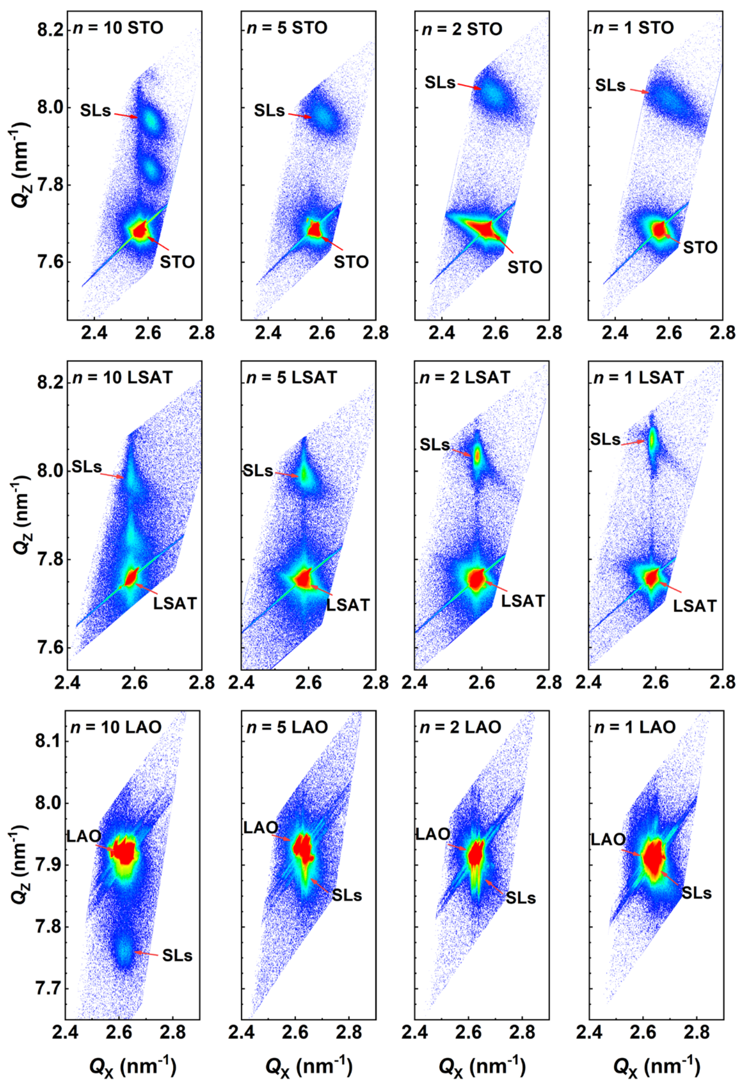

Fig. S4 Reciprocal space mappings of the (103) reflection for the $(PCO)_n/(CCO)_n$ SLs on various substrates. The SLs are fully strained by the LSAT and LAO substrates, but can partially relieve the strain when grown on STO substrates.

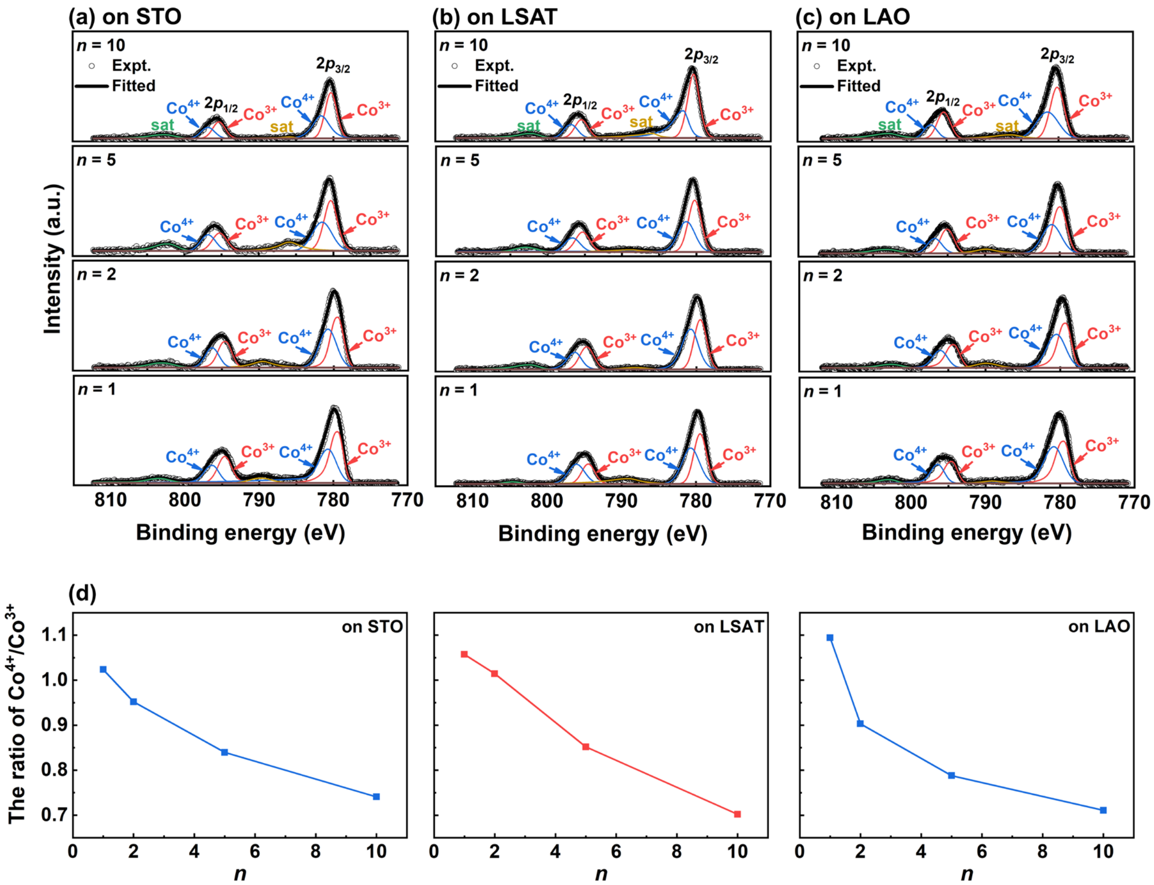

Fig. S5 (a)-(c) Co 2*p* XPS core level peaks of the $(PCO)_n/(CCO)_n$ SLs. (d) The calculated Co^{4+}/Co^{3+} ratio from the XPS results.

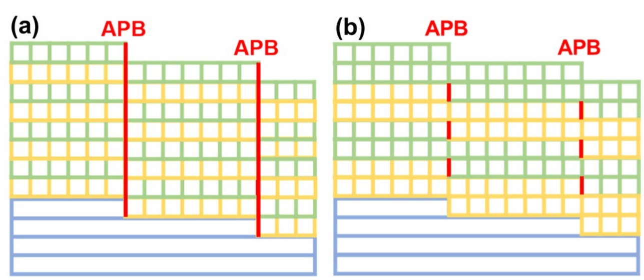

Fig. S6 Model of SL growth on (001) STO substrates for the (a) n = 1 and (b) n = 2 SLs.