Supplementary Information for “Dimensionality-Driven Insulator-Metal Transition in A-site Excess Nonstoichiometric Perovskites”

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Supplementary Methods

Crystal Structures of A'_{0.5}A_{n+1-0.5}B_{n}O_{3n+1} RP Superlattices

The whole family of ABO₃ superlattices, or the so-called homologous series, can be constructed by manipulating the perovskite-like slabs, and if possible by alternating them with various structural blocks of other types along a certain crystallographic direction. One of the most structurally simple series of such kind is the Srₙ₊₁TiₙO₃₊₁ or equivalently SrOₙSrTiO₃ (n = 1 to 5) Ruddlesden-Popper (RP) homologous series, all of which have a tetragonal symmetry within a space group of I4/mmm. The structures of these phases are characterized by intercalating a rock-salt SrO layer every n unit cell of SrTiO₃ perovskite along the [001] (c) direction. Consequently, this results in successive perovskite sheets being shifted by (1/2a, 1/2a) (a: in-plane lattice constant) with respect to each other along the basal plane of the layered structure (Supplementary Fig. S1). The known RP phases have already been confirmed to have nearly identical in-plane lattice constants, a and b (ranging slightly from 3.88 to 3.90 Å), but different out-of-plane
lattice constant, \( c \), for example, 12.60 Å for \( \text{Sr}_2\text{TiO}_4 \) \((n = 1)\), 20.38 Å for \( \text{Sr}_3\text{Ti}_2\text{O}_7 \) \((n = 2)\), 28.14 Å for \( \text{Sr}_4\text{Ti}_3\text{O}_{10} \) \((n = 3)\), 35.60 Å for \( \text{Sr}_5\text{Ti}_4\text{O}_{13} \) \((n = 4)\), and 43.50 Å for \( \text{Sr}_6\text{Ti}_5\text{O}_{16} \) \((n = 5)\), respectively\(^{35,37} \). Based on these pristine structures, the \( \text{La}_{0.5}\text{Sr}_{n+1-0.5}\text{Ti}_n\text{O}_{3n+1} \) \((n = 2 \sim 5)\) superlattices were fabricated by partially substituting the A-site ions (Sr) by the A' (La) ions in one rock-salt unit only\(^{38,39} \), although they are found to diffuse into the neighboring \( r \) sites in the films considered (Supplementary Fig. S1).

**Electronic States of the RP Phases with \( n = 2 \) and 3**

Calculations of electronic structures of the \( \text{La}_{0.5}\text{Sr}_{n+1-0.5}\text{Ti}_n\text{O}_{3n+1} \) superlattices with \( n = 2 \) and 3 were performed using the fully optimized geometries (Supplementary Fig. S1). For the purpose of comparison, the same cut-off energy of 400 eV, \( 4 \times 4 \times 1 \) \( k \) points, and the \( U \) and \( J \) values\(^{40,41} \) were applied, which ensured the total-energy convergence to less than 1 meV/atom. Supplementary Figure S2 presents total density of states (DOS) and the DOS projected on the specific atom species for the relaxed RP structures with \( n = 2 \) and 3. As in the case of \( n = 4 \), conduction band in both cases splits as well, which renders \( E_F \) stand in a gap between the fully occupied \( d_{xy} \) states and the remainder of \( d \) states. This resembles, to a large extent, the case of 2D confined Ti-\( d^1 \) Mott state\(^{42,43} \) and hence implies insulating nature in the both RP systems. Further analysis of band structures reveals that the split \( d_{xy} \) states arise from two parabola-like bands that are localized to within the two Ti layers proximal to the RP fault (Fig. 4a). The difference between the cases of \( n = 2 \) and 3 is that their overall PDOS features differ somewhat from each other, which can be attributed to the effect of the additional SrTiO\(_3\) unit cell. In addition, it is clear from Supplementary Fig. S2 that contribution to the CB comes predominantly from the Ti \( d \) states, and that the VB is dominated by the hybridized bonding states containing
mainly $p$ orbitals of O and $d$ orbitals of Ti.

**Nonequilibrium Quantum Electron Transport Properties**

The quantum transport properties through the La$_{0.5}$Sr$_{n+1}$Ti$_n$O$_{3n+1}$ ($n = 4$ and 5) are explored with the fully self-consistent nonequilibrium Green’s function method combined with the DFT, which is implemented in the Atomistix ToolKit (ATK) code. The reliability of this method has been tested, and the applicability of this code to the Pt–SrTiO$_3$–Pt heterostructure has also been examined in our previous report. The atomic and electronic structures of the semi-infinite electrodes are assumed to be the same as those of Pt bulk. On the other hand, electronic states of the scattering region are calculated self-consistently and atomic relaxation is also performed. The scattering region consists of perovskite RP layers and eight (4+4) surface layers of the left and right electrodes (Supplementary Fig. S3). The periodic boundary conditions are imposed in the directions parallel to the RP fault ($x$ and $y$ directions). The transmission function, $T(\varepsilon)$, is calculated using the formula,

$$T(\varepsilon) = \text{Tr}[G^r_C(\varepsilon)\Gamma_L(\varepsilon)G^a_C(\varepsilon)\Gamma_R(\varepsilon)],$$

where the $G^r_C$ and $G^a_C$ are the retarded and advanced Green’s function matrices of the scattering region, and the $\Gamma_L$ and $\Gamma_R$ are the spectral width functions of the left and right electrodes, respectively. With this equation, the transmission coefficient at $E_F$ for the $n = 4$ case is found to be rather small, though it is finite ($\sim 0.01 \times 2e^2/h$), which means electrons cannot permeate easily from the left Pt electrode to the right one, in accordance with the fundamental effect of the well localized states. Conversely, the transmission in the case of $n = 5$ increases substantially to 0.18, a manifestation of the opening of conduction channels. This value remains, however, far from one conductance unit ($G_0 = 2e^2/h$), thereby corroborating that not all electrons in the conducting RP contribute to the transport. Moreover, transmission
profiles in both cases differ substantially from each other, which is undoubtedly attributable to their essential differences in electronic states (Fig. 3).

**Local Bond Length Analysis**

Structural distortion may play an important role in the creation and stabilization of a Mott insulating state, and is hence one of the key factors in triggering an insulator-metal transition. The RP superlattice with \( n = 4 \), especially for the region neighboring to the fault, undergoes a distinct structural distortion that is intimately linked to the transition. As seen in Supplementary Fig. S4, the Ti-O distances on the TiO\(_2\) plane vary from 1.94 to 2.03 Å, which deviate severely from those in their calculated bulk counterparts, 1.98 Å\(^4\)\(^{,51}\). In addition, the La-Ti distances are also unbalanced, which are characterized by a prolonged length of 3.32 Å, accompanied by a shorter distance of 3.28 Å. This may provide a likely explanation for the presence of charge disproportionation on the Ti1 and Ti2 atoms (Fig. 4a). On the contrary, similar structural distortions are not observed in the RP phase with \( n = 5 \), which exhibits almost identical lengths for both the La-Ti and Ti-O bonds (with a bond-length variation of less than 0.01 Å). This change in the local structure of Ti ligand O from the Oh to C\(_{2v}\) breaks the crystal symmetry remarkably, which could stabilize the lowest, heavily split orbitals in the non-conducting RP phases. In general, a partially occupied, degenerate level is unstable against such a distortion, which results electronically in both the split of level and the lowering of the filled states, namely, the so-called Jahn-Teller (JT) effect. In such a localized Mott-Hubbard system, the coherent lattice distortions are unavoidable in order to lift the orbital degeneracy, which usually requires narrow bands, as we observed from the band structure.
Charge and Electrostatic Potential in the RP Phase with $n = 5$

The densities of electrons occupying the different perovskite layers are obtained by integrating the DOS from $E_F$ to the bottom of the conduction band as a function of the distance from center of RP fault. Like what was seen in Fig. 4d, charges are accumulated predominantly on the Ti layers (Supplementary Fig. S5a), but decay rapidly as one moves towards their adjacent SrO layers. This is ascribed to the wedge-shaped-like potential well presented at the Ti layers (see the arrows in Supplementary Fig. S5b), which in turn binds the La $d^1$ electrons into the Ti layers in an Airy-function-derived, localized wave function, as in case of the (SrTiO$_3)_n$(LaTiO$_3)_m$ superlattices$^{52}$. Furthermore, the amount of charge on the two Ti layers proximal to the fault is almost double in comparison to that on the Ti layers away from the fault, indicating that valence of the Ti atoms in these two layers is the most remarkably influenced by the La doping. It should be noted that a quantitative comparison of the magnitude of electron density with that of the potential is not reliable because the given potential is integrated at a global energy scale.
Supplementary Table S1| Energy for the relaxed RP phase with \( n = 5 \) after introducing an O vacancy into the different layer. Refer to Fig. 4b and Supplementary Fig. S1 for the definition of the sites.

| Upper Site | T3  | S3  | T2  | S2  | T1  | S1  |
|------------|-----|-----|-----|-----|-----|-----|
| Energy (eV)| -0.48 | -0.62 | -0.35 | -0.56 | -0.18 | 0.00 |

| Lower Site | T3’ | S3’ | T2’ | S2’ | T1’ | S1’ |
|------------|-----|-----|-----|-----|-----|-----|
| Energy (eV)| -0.48 | -0.62 | -0.35 | -0.55 | -0.19 | -0.01 |

Supplementary Figure S1| Schematic of crystal structures of unit cells with different dimensionality \( n \). The \( \text{La}_{0.5}\text{Sr}_{n+1-0.5}\text{Ti}_n\text{O}_{3n+1} \) Ruddlesden-Popper series with \( n = 1 \) (\( \text{La}_{0.5}\text{Sr}_{1.5}\text{Ti}_4\text{O}_{16} \)), \( n = 2 \) (\( \text{La}_{0.5}\text{Sr}_{2.5}\text{Ti}_2\text{O}_7 \)), \( n = 3 \) (\( \text{La}_{0.5}\text{Sr}_{3.5}\text{Ti}_3\text{O}_{10} \)), \( n = 4 \) (\( \text{La}_{0.5}\text{Sr}_{4.5}\text{Ti}_4\text{O}_{13} \)), \( n = 5 \) (\( \text{La}_{0.5}\text{Sr}_{5.5}\text{Ti}_5\text{O}_{16} \)), and \( n = \infty \) (\( \text{SrTiO}_3 \)) members. The \( \text{BO}_6 \) cages are represented by semi-translucent octahedra, where the Ti atoms sit at its center and the O atoms at its each apex. The atomic layers of \( \text{TiO}_2 \) and \( \text{SrO} \) are indicated by T and S, respectively.
Supplementary Figure S2|Total DOS and PDOS analysis. Similarity in electronic states between the La$_{0.5}$Sr$_{n+1-0.5}$Ti$_n$O$_{3n+1}$ phases with $n = 2$, 3, and 4. Total DOS and PDOS projected on the La, Ti, Sr, and O atoms for the relaxed RP with $n$ of (a) 2 and (b) 3. (c) PDOS of the Ti-3$d$ orbitals for the RP with $n$ of 2 and (d) that with $n$ of 3, where the PDOSs of the Ti $d_{xy}$ orbital are highlighted by shading.
Supplementary Figure S3|Schematic diagram of a two-probe Pt–La$_{0.5}$Sr$_n$–Ti$_n$O$_{3n+1}$–Pt heterostructure. The system has infinite extent in the [100] and [001] directions and extends to ±∞ in the [010] direction. Note that the transport calculations were only carried out for the RP phases with $n = 4$ and 5.
Supplementary Figure S4|Local bond-distance analysis of the RP phases with $n = 4$ (left) and 5 (right). Structural distortion is observed clearly in the non-conducting RP. The unit of distance is Å. The distances are shown only for the bonds adjacent to the fault.
Supplementary Figure S5|Charge and potential in the RP superstructure with $n = 5$.

(a) Planar-averaged total electron density along the [010] direction, which is integrated between the $E_F$ and the bottom of the conduction band. The T represents the TiO$_2$ layer, S the SrO layer, and the LS denotes the La$_{0.5}$Sr$_{0.5}$O layer. (b) Electrostatic potential as a function of distance from the center of RP fault along the [010] direction. The arrows mark the low potentials on each TiO$_2$ layer. The center of the RP fault is set to zero.
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