Direct visualization of ambipolar Mott transition in cuprate CuO$_2$ planes

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Identifying the essence of doped Mott insulators is one of the major outstanding problems in condensed matter physics and the key to understanding the high-temperature superconductivity in cuprates. We report real space visualization of Mott transition in Sr$_{1-x}$La$_x$CuO$_{2+y}$ cuprate films that cover the entire electron- and hole-doped regimes. Tunneling conductance measurements directly on the cooper-oxide (CuO$_2$) planes reveal a systematic shift in the Fermi level, while the fundamental Mott-Hubbard band structure remains unchanged. This is further demonstrated by exploring atomic-scale electronic response of CuO$_2$ to substitutional dopants and intrinsic defects in a sister compound Sr$_{0.92}$Nd$_{0.08}$CuO$_2$. The results could be better explained in the framework of self-modulation doping, similar to that in semiconductor heterostructures, and form a basis for developing any microscopic theories for cuprate superconductivity.

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High-temperature superconductivity in cuprates develops upon doping a state of matter that is insulating due to strong electron-electron correlation of CuO$_2$ plane (1-3). It is known that the ground state of cuprates as a Mott insulator could be well characterized by a charge-transfer gap (CTG) between charge-transfer band (CTB) and upper-Hubbard band (UHB), derived predominantly from the O 2$p$ and Cu 3$d_{x^2-y^2}$ orbitals, respectively (4, 5). Whether the doping prompts spectral weight transfer from the high-energy scale (6) and pins the Fermi energy ($E_F$) by some putative midgap states within CTG (4, 5, 7) or it induces $E_F$ shift of the Mott-Hubbard insulating state (8-10) is a fundamental question but remains unresolved. The difficulty of settling this open issue is partially owing to specific doping level (4, 10) or limited doping range of samples (5, 9) explored in previous experiments, partially to the complex layered structure of cuprates. The latter makes direct experimental access to the CuO$_2$ planes that are sandwiched between the charge reservoir layers extremely challenging, which becomes prominent for surface-sensitive techniques (4, 5, 9-11). Under this context, the systematic measurement of a cuprate system covering sufficiently broad doping range and both electron ($n$)- and hole ($p$)-doped regimes (12), and meanwhile on the CuO$_2$ planes is the most effective way to solving this major problem.

We report such measurement by choosing an infinite-layer SrCuO$_2$ compound, because, besides its simplest crystal structure among cuprates (see Fig. 1A, inset), its surface is terminated with the CuO$_2$ plane (13-15). Given the metastability of bulk infinite-layer cuprates, an ozone-assisted molecular beam epitaxy technique is utilized to prepare single-crystalline films of Sr$_{1-x}$La$_x$CuO$_{2+y}$ (SLCO) and Sr$_{0.92}$Nd$_{0.08}$CuO$_2$ (SNCO) with well-controlled dopant type and concentration (16). This control enables us to access the entire doping regime in the phase diagram and investigate the Mott physics on CuO$_2$ comprehensively.

The detailed structural characterizations of SLCO samples are illustrated in Fig. 1. Shown in Fig. 1A are a series of X-ray diffraction (XRD) patterns of SLCO films with La doping level $x$ from 0, 0.054, 0.061, 0.076, 0.100, 0.104, 0.110, 0.132, 0.167 to 0.206. The good crystallinity is evident by the distinct Kiessig fringes surrounding the main diffraction peaks of SLCO films (fig. S1). Quantitative analysis of the XRD data reveals two distinct phases: a phase with $c$-axis lattice constant of $c \sim 0.345 - 0.350$ nm for $x < 0.104$ and another with $c$-axis lattice constant of $c \sim 0.365$ nm for $x > 0.132$, while for $x = 0.104$ to 0.132 the two phases coexist, as
summarized in Fig. 1B. Both phases belong to the family of infinite-layer cuprates sharing the same crystal structure, except for a small difference by \( \sim 0.2 \) Å in the \( c \)-axis lattice constant \((17, 18)\). Yet, the Hall effect measurements reveal that the two phases exhibit \( n \)-type (electron) and \( p \)-type (hole) conductivity, respectively, involving a carrier-sign reversal at \( x \sim 0.104 - 0.132 \) (fig. S2). Similar phenomenon was evidenced in electron-doped \( \text{La}_{2-x}\text{Ce}_x\text{CuO}_4 \) \((19)\), but the mechanism differs radically from each other (Supplementary section 1). For convenience, we label the two phases as \( n \)-SLCO and \( p \)-SLCO, as indicated by the blue and black arrows, respectively, in Fig. 1A.

The phase identification and atomically sharp interface in SLCO/SrTiO\textsubscript{3} heterostructures are further established by high-resolution scanning transmission electron microscopy (STEM). By applying a new integrated differential phase contrast-STEM imaging technique \((20)\), we show in Fig. 1C and 1D that the variation of \( c \)-axis lattice constant and concomitant carrier-sign reversal are due to the appreciable intake of apical oxygen (see the red and green arrows in Fig. 1D) as \( x > 0.132 \). We also carry out \textit{in-situ} scanning tunneling microscopy (STM) imaging of the SLCO films. The \( n \)-SLCO cuprate films display a pristine \( \text{CuO}_2 (1 \times 1) \) surface with the anticipated Cu-Cu spacing of approximately 3.9 Å (Fig. 1E), whereas the \( p \)-SLCO ones are characteristic of a \( (2 \times 2) \) superstructure (Fig. 1F). The observed \( (2 \times 2) \) superstructure in \( p \)-SLCO is consistent with the periodic occupation of apical oxygens, whereas the integrity of \( \text{CuO}_2 \) planes is well maintained (Supplementary section 2, Fig. 1D and fig. S3). The excellent consistency among XRD, STEM, STM and Hall effect measurements indicates that a system for exploring the physics of doped Mott insulator directly on \( \text{CuO}_2 \) planes has been prepared.

Our most significant finding is that the fundamental Mott-Hubbard bands remain essentially unchanged, while the \( \varepsilon_r \) systematically moves with doping. We reveal this feature unambiguously by measuring the electronic density of states (DOS) of \( \text{CuO}_2 \) planes at various doping levels via STM, as enumerated in Fig. 2, A to C and fig. S4. What becomes immediately obvious is the overall similar electronic structure: a CTG between CTB (its onsets are marked by black triangles) and UHB (its onsets are marked by blue triangles) is invariably present with the aid of the schematic band structure (insets of Fig. 2, B and C). Figure 2D depicts the onset energies of CTB and UHB as a function of the La doping level \( x \) (top panel), from which the magnitude \( \Delta_{\text{CT}} \) of CTG separating CTB and UHB is extracted (middle panel). Here the onsets of
CTB (UHB) are determined from the intersections of linear fits to the data above and below the CTB (UHB) (fig. S4B). Except for the undoped (x = 0) and slightly doped (x = 0.020) samples (fig. S5) for which the $\Delta_{CT}$ cannot be measured correctly by STM due to the tip-induced band bending (21), we find that the $\Delta_{CT}$ is essentially doping-independent and held constant at 1.30 ± 0.07 eV, irrespective of either samples at various La doping (Fig. 2D) or a sample over various regions (fig. S4D). This value is close to the gap size of ~ 1.5 eV measured by optical conductivity on the infinite-layer cuprates (22). Furthermore, the bandwidths of CTB and UHB have a value of approximately 0.46 eV irrespective of doping (fig. S6), which is in good agreement with the previously reported value of 0.41 eV (14). Altogether, we conclude that the doping doesn’t disrupt the fundamental band structure of the CuO$_2$ planes in the SLCO cuprate films we have investigated. Such finding accords nicely with the stability of Mott-Hubbard bands with the Sr doping up to x = 0.3 in La$_{2-x}$Sr$_x$CuO$_4$ cuprates (23).

As anticipated but not yet confirmed in previous experiments, the $E_F$ of undoped SLCO cuprates is found to lie at the midgap energy ($E_i$, the vertical bars in fig. S5). With increasing La doping from x = 0.020 to 0.054, 0.061, 0.076 and 0.100, the $E_F$ moves progressively away from the $E_i$ (refer to the right-pointing arrows in Fig. 2, A and B) and gradually approaches the UHB, consistent with $n$-type doping. On the other hand, at x = 0.132, the $E_F$ suddenly jumps down below $E_i$ (see the left-pointing arrows in Fig. 2, A and C) and even passes into the CTB because of the intake of apical oxygen (Fig. 1D), signifying a transition to $p$-type doping. As the x is further increased, the $E_F$ shifts upwards again (Fig. 2A and the bottom panel of Fig. 2D), a combined consequence of increased La donors and reduced apical oxygen (Supplementary section 1). Considering that the only difference between $n$-SLCO and $p$-SLCO samples is the type of dominant ionized dopants, and that all STM measurements are conducted on the CuO$_2$ planes, this systematic shift of $E_F$ with doping should be inherent to doped Mott insulators.

We argue that the above findings on CuO$_2$ are of fundamental importance and contrast sharply with both scenarios of the $E_F$ pinning by the midgap states (4-7, 21) and collapsing of the Mott-Hubbard ground state upon doping iridates (24), which were distinctively measured on the charge reservoir layers. Instead, our results bear great resemblance to the modulation doping of Al$_x$Ga$_{1-x}$As/GaAs semiconductor heterostructures (25), with the roles of the valence and conduction bands of the undoped GaAs played by the CTB and UHB of the chemically
undisturbed CuO in SLCO, respectively. The minor distinction is that for SLCO the separation of ionized dopants (La and apical oxygen) in the intervening Sr layers and free carriers in CuO occurs in SLCO itself, for which it is best described as self-modulation doping (26). In this scheme, the fundamental band structure of the stoichiometric CuO and GaAs does not alter with doping in a fundamental fashion (27), although the cause of insulating gap by electron correlations in CuO sounds so different than the band theory in conventional semiconductors. The uppermost role of La (O) dopants is that they provide electron (hole) charges for the CuO planes so as to push the $E_f$ upwards (downwards). These happen to be what we have clearly observed in Fig. 2.

The key finding of unchanged Mott-Hubbard band structure of CuO against the dopants is further proved by studying SNCO cuprates. As compared to SLCO, the SNCO compounds have a smaller lattice mismatch with the SrTiO$_3$ substrate during heteroepitaxy (28), since the trivalent dopant ions of Nd$^{3+}$ (1.25 Å) are smaller than La$^{3+}$ (1.30 Å). This leads to an essentially atomically flat topography of CuO (Fig. 3A) and spatially more uniform conductance $dI/dV$ spectra (Fig. 3B), in Sr$_{0.92}$Nd$_{0.08}$CuO$_2$ samples (fig. S7). Evidently, the overall electronic structure, measured $\Delta_{\text{CT}} \sim 1.28 \pm 0.04$ eV and bandwidths of CTB (0.43 ± 0.06 eV)/UHB (0.46 ± 0.14 eV) resemble with SLCO in a prominent way. The observations convincingly affirm the immunity of the Mott-Hubbard band structure of CuO to the dopant type (La, Nd and O) in the intervening Sr planes (or saying charge reservoir layers), echoing the above self-modulation doping scenario.

Furthermore, the local response of electronic DOS to single dopants or impurities provides additional atomic-scale insight into the self-modulation doping scheme. In Fig. 3, C to H, we explore a single substitutional Nd donors (Nd$_{sr}$), intrinsic acceptors of apical oxygen (O$_a$) and Cu vacancy (V$_{Cu}$), as well as the nearby electronic DOS by acquiring the space-dependent $dI/dV$ spectra. The occurrence of O$_a$ and V$_{Cu}$ acceptors may be prompted by their reduced formation entropies as the $E_f$ is lifted by the Nd$_{sr}$ dopants (29). In the vicinity of Nd$_{sr}$ donors, both CTB and UHB are shifted downwards (Fig. 3D), whereas the O$_a$ and V$_{Cu}$ acceptors locally move the bands upwards (Fig. 3, F and H). Such a band bending accords with screened Coulomb potential (fig. S8 and Supplementary section 3). Although the V$_{Cu}$ acceptors significantly suppress the UHB on a length scale of 4.3 Å (Fig. 3H and fig. S8D), the whole Mott-
Hubbard bands of CuO$_2$ are robust against the Nd$_{Sr}$ and O$_{A}$ defects in the charge reservoir layers of Sr (Fig. 3, D and F). The observations not only reveal the unique identity of electronic DOS around 0.5 eV as the UHB of Cu orbitals, but also imply that the Mott-Hubbard bands of SNCO are solely sensitive to the $V_{Cu}$ defects on the CuO$_2$ planes.

The unchanged Mott-Hubbard band structure of cuprates against the defects of charger reservoir layers is corroborated by acquiring the $48 \times 48$ grid dI/dV spectroscopy data over a field of view of 62 Å $\times$ 62 Å, devoid of any defects in the topmost CuO$_2$ plane (Fig. 4A, inset). The Nd$_{Sr}$ donors and O$_{A}$ acceptors underneath are spatially distributed randomly, which locally enhance and suppress the top Cu atoms, respectively. As shown in Fig. 4A, the electronic DOS display apparently spatial variation in the onsets of UHB and CTB, but the overall Mott-Hubbard band structure change little, which are quantitatively revealed in Fig. 4, B and C. On the bright regions, the UHB and CTB onset energies, which correlate positively with each other (top panel of Fig. 4B), appear lower, matching fairly well with the aggregation of Nd$_{Sr}$ donors there. Note that the tiny spatial variation in $\Delta_{CT}$ (bottom panel of Fig. 4B and Fig. 4C) may arise from either the measurement uncertainty or the heavy-doping-associated band tailing (30), or both.

Followed by the systematic shift in $E_{F}$, we observe dopant-induced in-gap states (IGS) that overspread the whole CTG (Fig. 2, A to C, Fig. 3 and Fig. 4A) and induce a Mott insulator-metal transition. As plotted in fig. S9 are the $x$-dependent lower-energy-scale conductance spectra near $E_{F}$. Intriguingly, we reveal smoothly varying electronic DOS harboring nanoscale puddles of pseudogap (fig. S9B), separated spatially by other regions that are relatively featureless (fig. S9C). The pseudogaps are characteristic of a pronounced electron-hole asymmetry that awaits further explanation (Supplementary section 4 and fig. S10). Nevertheless, in contrast to earlier STM studies of charge reservoir layers (e.g. BiO, CaCl and SrO) in cuprate compounds (4, 5, 31) and iridates (21, 32), no peak or hump-like electronic DOS have been observed within the CTG of CuO$_2$ planes. We therefore argue that this finding is not expected from the emergent IGS associated with spectral weight transfer from the high- to the low-energy scale (6). From the viewpoint of modulation-doping scheme in semiconductor physics (25), the dopant-induced continuum of IGS could be better explained invoking the confined two-dimensional electron gas at the very Sr$_{1-x}$(La, Nd)$_x$/CuO$_2$ interfaces, evanescent states in the charge-transfer gap of
CuO$_2$ (27), or a combination between them. The present experimental data are not sufficient enough to confirm either scenario, and the nature of emergent IGS responsible for the low-lying physics in cuprates remains an open question.

To conclude, our direct measurement of Mott insulator-metal transition on the CuO$_2$ planes – the key building blocks of copper-oxide superconductors, has presented several complementary and exceptionally new results, compared with earlier studies that were usually conducted on the charge reservoir layers of cuprates. The observed robust fundamental Mott-Hubbard bands against doping and the self-modulation doping-driven systematic shift of $E_F$ should form a starting point for developing any microscopic models of the Mott physics as well as the superconductivity mechanism in cuprates. Such a model might be applicable to a number of other layered and strongly correlated materials, i.e. iron pnictides and iridates (33), which merits a future study.
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**Figure captions**

*Fig. 1. Structural characterizations of SLCO epitaxial films.* (A) X-ray diffraction spectra for Sr$_{1-x}$La$_x$CuO$_{2+y}$ films (~60 unit cells) with varying x. The blue and black arrows denote the reflection peaks from n-SLCO and p-SLCO, respectively, whereas the green dashes mark the signals from the SrTiO$_3$ substrates. Inset shows the schematic crystal structure of SLCO. (B) Out-of-plane lattice constant c as a function of the La doping level x. The two phases of n-SLCO and p-SLCO, coexisting for 0.104 < x < 0.132, are represented by the empty circles and squares. (C and D) Integrated differential phase contrast-STEM images of n(p)-SLCO/SrTiO$_3$ heterostructures, enabling simultaneous visualization of the heavy (Sr, La and Cu) and light (O) atoms. The two horizontal dashes mark the interfaces of SLCO/SrTiO$_3$. Inserted in D is a zoom-in of the p-SLCO/SrTiO$_3$ interface. Colored atoms have been partly superimposed on n(p)-SLCO films. In contrast to n-SLCO without apical oxygen, an excess of oxygen (marked by the red and green arrows) are found to register at the apical sites of Cu and change alternately in intensity and shape in p-SLCO cuprates, while the planar oxygen (marked by the orange arrows) in the CuO$_2$ planes exhibits no spatial variation. (E and F) Representative STM topographic images (80 Å × 80 Å) of n-type (x = 0.076) and p-type (x = 0.167) SLCO films. Tunneling conditions are (E) $V = -1.0$ V, $I = 10$ pA and (F) $V = -0.3$ V, $I = 50$ pA. Note that the unit cells outlined by the white squares and rectangles become doubled in size for p-SLCO as compared with n-SLCO.

*Fig. 2. Robust Mott-Hubbard bands on CuO$_2$.* (A) Spatially averaged differential conductance $dI/dV$ spectra revealing the electronic structure of SLCO films under various doping. Gray solid lines and bars indicate the $E_F$ and midgap energy $E_i$ throughout. For each $dI/dV$ spectrum, the tunneling junction is stabilized to the starting voltage from the negative side and $I = 100$ pA except for $x = 0.132$ and 0.167 ($I = 200$ pA). (B and C) Representative space-specific $dI/dV$ conductance spectra of n-SLCO ($x = 0.100$) and p-SLCO ($x = 0.206$). Setpoint: (B) $V = -1.6$ V, $I = 100$ pA; (C) $V = 1.8$ V, $I = 200$ pA. Inserted are schematic energy bands of cuprates, with only the CTB (green) and UHB (unfilled) shown. The measured electronic DOS matches nicely with the fundamental band structure of CuO$_2$, except for the doping-induced IGS. (D) Statistically measured onset energies for CTB and UHB (top panel), charge-transfer gap $\Delta_C$ (middle panel) and $E_F$ shift as relative to $E_i$ (bottom panel) versus the La doping level x. The standard
deviations from $dl/dV$ measurements over various regions are smaller than the symbol size.

**Fig. 3. STM around single defects.** (A) STM topography of SNCO cuprate films (40 Å × 40 Å, $V = 1.5$ V, $I = 20$ pA) showing the atomically flat surface of CuO$_2$. (B) Differential conductance $dl/dV$ spectra acquired at equal separation along a trajectory of 26.5 Å on the CuO$_2$ planes. Inserted is the schematic band structure of pristine cuprates. The black and red dashes mark the onsets of UHB and CTB, respectively. (C and D) Atomic-resolution topography (20 Å × 20 Å, $V = -1.4$ V, $I = 20$ pA) of a single Nd$_{Sr}$ dopant and $dl/dV$ spectra taken at equal separations along a trajectory of 16.4 Å from the Nd$_{Sr}$ (indicated by the bottom curve). The substitution of Sr$^{2+}$ by trivalent Nd$^{3+}$ ion is found to brighten four neighboring Cu atoms at the top CuO$_2$ plane, denoted by the orange dots. (E and F) Atomic-resolution STM topography (20 Å × 20 Å, $V = 1.0$ V, $I = 20$ pA) of an intrinsic O$_A$ acceptor and $dl/dV$ spectra taken at equal separations along a trajectory of 12.2 Å from its center (bottom curve). The O$_A$ acceptors somewhat depress the top Cu atoms, but never destroy the integrity of CuO$_2$ planes. (G and H) STM topography (20 Å × 20 Å, $V = 1.5$ V, $I = 20$ pA) of an intrinsic Cu vacancy ($V_{Cu}$) and $dl/dV$ spectra taken at equal separations along a trajectory of 12.8 Å from its center (bottom curve). The setpoint for all $dl/dV$ conductance spectra is stabilized at $V = 1.5$ V and $I = 50$ pA.

**Fig. 4. Mapping of Mott-Hubbard states.** (A) Local DOS spectra along the white arrow of the inserted STM topography (62 Å × 62 Å, $V = 0.4$ V, $I = 20$ pA), with randomly distributed Nd$_{Sr}$ donors and O$_A$ acceptors in the underlying Sr layer. Every curve is the mean of 16 $dl/dV$ spectra inside the color-coded square. For clarity the curves have been vertically offset by 0.05 nS. (B) Correlations between the extracted UHB onsets (top panel), $\Delta_{CT}$ (bottom panel) and CTB onsets. (C) Maps of the extracted UHB onsets, LHB onsets and $\Delta_{CT}$. Note that the energy ranges coded by the same color palette change from ~0.5 eV for UHB to 0.43 eV for CTB and 0.33 eV for $\Delta_{CT}$. 
Figure 1
Figure 2
Figure 3
Supplementary Online Materials for

Direct visualization of ambipolar Mott transition in cuprate CuO$_2$ planes

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This supplement includes:

Materials and Methods
Supplementary Text
Figs. S1 to S10 and Captions
Materials and Methods

Sample growth. High-quality $\text{Sr}_{1.4}\text{La}_{0.6}\text{CuO}_{2+y}$ (SLCO) and $\text{Sr}_{0.92}\text{Nd}_{0.08}\text{CuO}_2$ (SNCO) epitaxial films were prepared in two ozone-assisted molecular beam epitaxy (O-MBE) chambers, every of which is equipped with a quartz crystal microbalance (QCM, Inficon SQM160H) for accurate flux calibration. Atomically flat $\text{SrTiO}_3(001)$ substrates with 0.05 wt% Nb doping were cleaned by heating up to 1200°C under ultrahigh vacuum (UHV) conditions for 20 minutes, leading to a TiO$_2$ termination. All epitaxial cuprate films for STM studies were prepared on the doped $\text{SrTiO}_3$ substrates. For transport and Hall measurements, the insulating $\text{SrTiO}_3(001)$ substrates were used to prepare $p$-type SLCO films, while the $n$-type SLCO film ($x = 0.097$) was grown on ScO$_2$-terminated DyScO$_3(110)$ substrate, which was pre-cleaned by annealing in oxygen at 1000°C for 6 hours and then etching in 12 mol/L NaOH solution for 30 minutes. As oxidant, the distilled ozone flux was injected from our home-built gas delivery systems into the O-MBE chambers via a nozzle 50 mm away from the substrates. All the epitaxial films were grown by co-evaporation of high-purity metal sources (La/Nd, Sr and Cu) from standard Knudsen cells under an ozone flux beam of $\sim 1.5 \times 10^{-5}$ Torr and at an optimized substrate temperature $T_{\text{sub}}$ of $550^\circ\text{C} \sim 580^\circ\text{C}$. The lower ($< 500^\circ\text{C}$) and higher $T_{\text{sub}}$ ($> 600^\circ\text{C}$) were found to either degrade severely the SLCO and SNCO film crystallinity or result in other unwanted phases. After growth, the samples were annealed in UHV at the same $T_{\text{sub}}$ for 30 minutes and then gradually cooled down to room temperature.

In order to ensure the stoichiometry of SLCO/SNCO films, the beam flux of the metal sources was precisely calibrated in sequence prior to every film growth, yielding a growth rate of approximately one unit cell per minute. The XRD measurements reveal that the infinite-layer SrCuO$_2$ can be synthesized only at 1:1 flux ratio of Sr to Cu. Further addition of La/Nd reactants leads to substitution of trivalent La/Nd for divalent Sr in the intervening layers and the formation of SLCO/SNCO cuprate films. The doping level $x$ is determined by in-situ QCM. Moreover, we model the satellite peaks (Kiessig fringes) in the XRD spectra (fig. S1 and fig. S7B) and estimate the film thickness, which shows a pretty good agreement with the nominal thickness determined by QCM-measured flux of Cu and growth duration. The SLCO samples investigated are typically 60 unit cells ($\sim 20 \text{ nm} – 23 \text{ nm}$) in thickness to preserve consistency.
**In-situ STM measurements.** All STM measurements were carried out in Unisoku USM 1300S 3He systems at a fixed temperature of 4.2 K, which are connected to the O-MBE chamber. The base pressure is better than $1.0 \times 10^{-10}$ Torr. Polycrystalline PtIr tips were cleaned via e-beam heating in UHV, calibrated on MBE-prepared Ag/Si(111) films, and then used throughout the experiments. All STM topographies were acquired in constant current mode with the voltage applied on the sample. The differential conductance $dI/dV$ spectra and maps were measured by using a standard lock-in technique with a small bias modulation. Special measures such as grounding and shielding were performed to increase the stability and spectroscopic resolution ($\sim 1.0$ meV) of our STM systems.

**Ex-situ XRD, STEM and Hall measurements.** After in-situ STM characterization, we transferred the samples out of the UHV chamber for ex-situ XRD, STEM and Hall measurements. The XRD measurements were carried out with a high-resolution diffractometer (Rigaku, Smartlab) using the monochromatic Cu K$_{\alpha1}$ radiation ($\lambda = 1.5406$ Å). We then investigated the crystalline structures with high resolution STEM, operated in both high-angle annular dark field (HAADF) and the recently introduced integrated differential phase contrast modes (20). The cross-sectional sample for observation in electron microscope were prepared by focused ion beam milling with a Ga ion beam at 30 kV on a Zeiss Auriga workstation, followed by thinning with low energy Ar$^+$ in a Bal-Tec Res-120 ion beam milling system to remove the damaged surface layers. The atomically resolved HAADF-STEM and integrated differential phase contrast-STEM experiments were carried out on a Thermo Fisher Scientific Titan Themis microscope at 300 kV, equipped with a high-brightness Schottky field emission electron gun, a probe Cs corrector and a segmented DF4 detector with 4 quadrants, at room temperature. The available point resolution is better than 0.6 Å. Hall measurements were performed in a closed-cycle system (Oxford Instruments TelatronPT), equipped with a He-3 insert. The temperature sensor was placed directly below the sample stage and in a configuration with the minimal magnetoresistance. Freshly-cut indium cubes were cold pressed onto the samples as contacts. Standard lock-in technique was utilized to measure the transverse and longitudinal resistances in a six-terminal configuration with a typical excitation current of 1 µA at 13 Hz.

**Supplementary Text**

**Section 1: Hall measurements**
We have performed Hall measurements to exploit the doping dependence of carrier type
and density \( n \) in the MBE-prepared SLCO cuprates. In line with previous study (17), the SLCO
film grown directly on SrTiO\(_3\) is non-superconducting from electrical transport measurements,
enabling us to conveniently determine \( n \) that amounts to the Hall number \( n_H \) at the low-\( T \) limit.
Our measurements of the transverse Hall resistivity \( \rho_{xy} \) on four SLCO films with La content \( x = 0.097, 0.153, 0.167 \) and 0.194, as well as the calculated Hall coefficient \( R_H \) from the slope of a
linear fit to data (gray lines), are summarized in fig. S2. The type of dominant carriers, inferred
from the sign of \( R_H \), changes from electron-like to hole-like as the La doping level exceeds \( x \sim 0.132 \). At \( x = 0.097 \), the absolute value of \( R_H \) in SLCO film drops with reducing temperature
until it gets saturated at low \( T \), analogous to electron-doped La\(_{2-x}\)Ce\(_x\)CuO\(_4\) cuprates (19).
Assuming a single-band model, we calculate the carrier density \( n \sim n_H = 0.08 \) electron per
planar Cu, close to the nominal La doping level \( x = 0.097 \). This is understandable because
substituting each trivalent La ion for divalent Cu ion, if fully ionized, is expected to donate one
electron. In the samples with \( x > 0.132 \), we instead see that \( R_H \) alters little with \( T \) over the full
temperature range and the low-\( T \) \( R_H \) shrinks abruptly by nearly one order of magnitude,
indicative of heavy hole doping of \( n_H = 0.83, 0.50 \) and 0.48 hole per planar Cu for \( x = 0.153, 0.167 \) and 0.194 samples, respectively.

At first glance, the above findings accord phenomenally with those previously reported
in electron-doped La\(_{2-x}\)Ce\(_x\)CuO\(_4\) (19), in which the carrier density \( n \) changes from \( n = 1 - x \) at
high doping to \( n = -x \) at low doping, associated with a Fermi surface reconstruction by the
antiferromagnetic order below a critical doping. However, a quantitative comparison yields
substantial deviation of the measured \( n_H \) from the expected \( n = 1 - x \) for the two samples with
\( x = 0.167 \) and 0.194. An explanation of this discrepancy by oxygen vacancies, as suggested in
La\(_{2-x}\)Ce\(_x\)CuO\(_4\) (19), seems be highly improbable in our case, because the high-resolution STEM
measurements of \( p \)-type SLCO samples reveal a large number of apical oxygen in the Sr
intervening planes, with the oxygen atoms in the CuO\(_2\) planes little disturbed (Fig. 1D). Given
that an apical oxygen contributes two holes, the Fermi surface reconstruction picture is almost
incompetent to describe the \( x \)-dependent Hall coefficient \( R_H \) in SLCO films.
Considering the possible coexistence of electron carriers by La dopants and hole carriers by apical oxygen, we interpret the $R_H$ using a simple “two-band model” and derive an expression for the measured $R_H$ as

$$R_H = \frac{1}{|q|} \frac{n_h \mu_h^2 - n_e \mu_e^2}{(n_h \mu_h + n_e \mu_e)^2},$$

where $q$, $n_e(h)$ and $\mu_e(h)$ represent the elementary charge, $e(h)$ carrier density and mobility, respectively. Although the $\mu_e(h)$ motility is unknown, an increase of $n_e$ would result in smaller $R_H$ at a fixed $n_h$, contradictive to our observation in fig. S2D. This implies that the apical oxygen might vary or more precisely decrease in number from $x = 0.153$ to $x = 0.197$, which matches excellently with the upward shift of $E_F$ with increasing $x$ (Fig. 2, A and D). On the other hand, for the super-oxygenated SLCO films the Fermi level $E_F$ lies far away from the La dopant energy levels (close to UHB) and most La donors might be not ionized. Under this context, the free mobile carriers are predominantly holes contributed by the apical oxygen. Thus, the increased $R_H$ is in line with reduced apical oxygen with increasing La doing level $x$ as well.

Section 2: STEM of $p$-SLCO cuprate films

Unlike $n$-SLCO cuprate films with well-defined atomic configuration (Fig. 1C), the HAADF-STEM images of $p$-SLCO samples reveal apparent variations of Sr and Cu atomic columns in both of their intensity and shape. As evident in fig. S3, the variation comprises an atomic column with a round shape and higher intensity (marked by the red and white arrows) followed by another consecutive atomic column with a dumbbell-like shape and lower intensity (marked by the green and yellow arrows) when considered for Cu along all the in-plane high-symmetry axes ([100], [010] and [110]) and for Sr solely along the diagonal directions, forming a $2 \times 2 \times 1$ superstructure. This is compatible with the $2 \times 2$ surface structure by STM imaging of $p$-SLCO (Fig. 1F), in which the Cu atomic distortions might modify their equivalence and render three quarters of the top Cu atoms invisible for STM. A simultaneous visualization of heavy (Sr/Cu) and light atom (O) by an iDPC-STEM technique (20) enables the Sr and Cu atomic distortions to be correlated with the intake of excess oxygens at the apical sites of Cu atoms (cf. Fig. 1C and Fig. 1D). Actually, the apical oxygens are found to change alternately the intensity and shape as well. Notably, the planar oxygen atoms in the CuO$_2$ planes remain little disturbed and exhibit no observable distortion (orange arrows in Fig.
1, C and D). As thus, our SLCO samples differ sharply from the SLCO cuprate films prepared by pulsed laser deposition, which exhibits an oxygen-deficient $2\sqrt{2} \times 2\sqrt{2} \times 2$ superstructure (18). Clarifying this discrepancy lies beyond the scope of the present study. We highlight that our MBE preparation and doping control of the super-oxygenated SLCO films have led to $\rho$-SLCO cuprate films, allowing for a direct comparison study between them and the $n$-type ones, both sharing the same infinite-layer crystal structure.

**Section 3: Screening of ionized dopants and defects**

In order to quantify the response of Mott-Hubbard bands to Nd$_{Sr}$, O$_A$ and V$_{Cu}$, we present the extracted onset energies of CTB and UHB as well as their separation $\Delta_{CT}$ as a function of lateral distance $d$ from each defect in fig. S8. Intriguingly, the $\Delta_{CT}$ remains constant within the measurement uncertainty (see the top panels of figs. S8, A and B), irrespective of the presence of Nd$_{Sr}$ donors and O$_A$ acceptors in charge reservoir layers. This echoes our claim that doping the charge reservoir layers does not substantially modify the Mott-Hubbard band structure of CuO$_2$ planes, although the $E_s$ is locally shifted upwards/downwards when approaching the donors/acceptors. However, a closer examination reveals an apparent distinction in the site-dependent evolution of UHB and CTB. As for the positively charged Nd$_{Sr}$ donor, the onset energies of UHB and CTB rise abruptly when leaving away from their centers (fig. S8A), which can be approximated with a screened Coulomb potential via $\frac{1}{r}e^{-r/R_b}$ (red curves in the middle and bottom panels of Fig. S8A). Here $R_b$ represents the screening length, and the radial distance $r = \sqrt{d^2 + (c/2)^2}$ is measured from the position of Nd$_{Sr}$ donor. In contrast to the Nd$_{Sr}$ donors, around which the accumulated charges originate from free electron carriers that are mobile in $n$-type SNCO cuprates, the negatively charged O$_A$ acceptors are screened from spatially fixed and ionized Nd$_{Sr}$ donors. This agrees nicely with a slow descending of UHB and CTB with increasing $d$, exemplified by the quadratic lines (red curves) in the middle and bottom panels of fig. S8B.

Unlike the roles played by either Nd$_{Sr}$ or O$_A$, the UHB becomes significantly suppressed in the vicinity of V$_{Cu}$ (Fig. 3H). Consequently, there exists no way to deduce the onset energies of UHB and $\Delta_{CT}$. Despite this limitation, the site-dependent CTB onsets could still be extracted in fig. S8C. In analogy to O$_A$, the V$_{Cu}$ acceptor also results in a slowly descending CTB when leaving
away from its center (red curve in fig. S8C), because the ionized Nd$_{Sr}$ donors responsible for the electrostatic screening cannot squeezed as the mobile electron charges. By normalizing all spectra to their mean dI/dV value, we extracted the space-dependent UHB spectral weights as the integration of the local DOS over the UHB energy range. As revealed clearly from fig. S8D, the spectral weight of UHB decays rapidly toward V$_{Cu}$ in an exponential way. The resultant decay length of 4.3 Å appears comparable to the Cu-Cu spacing of 3.93 Å.

Section 4: Low-lying electronic DOS

Accompanied by the dopant-driven Mott insulator-metal transition, a number of low-lying electronic states emerge and overspread the whole CTG (Fig. 2, A to C, Fig. 3 and Fig. 4). By examining the space-dependent dI/dV conductance spectra at the lower energy scale (-90 meV ~ 90 meV), many nanoscale patches of pseudogap (~ 50%, fig. S9B) or U-shaped gap (~ 10%, not shown) develop ubiquitously from regions with populated IGS (the bright regions in fig. S9A), whereas the electronic DOS exhibit no gap opening on the relatively darker regions (fig. S9C). We here ascribe this pronounced spatial variations to the electronic inhomogeneity, which have been routinely observed in cuprates (5, 31) and iridates (21, 32). Indeed, in either region, the dI/dV spectra are very of spatial inhomogeneity (fig. S9, B and C), regardless of the doping level $x$. Notably, some of the pseudogap-like spectra exhibit clear coherence peaks, presenting no distinction from the superconducting cuprate compounds (11). This hints at local superconductivity in the SLCO epitaxial films, and their discontinuity may be the primary cause for the absent macroscopic superconductivity from electrical transport measurements (17). Note that the bright puddles correspond to the regions with more carriers, consistent with the atomic-scale STM studies of SNCO films (Fig. 3 and Fig. 4).

More remarkably, we find that every spectrum in fig. S9, B and C has a sloped background (to wit, electron-hole asymmetry) that differs radically between the n-SLCO and p-SLCO films. We reveal this dichotomy more clearly by spatially averaging the dI/dV spectra on the pseudogap regions as a function of $x$, plotted in fig. S10A. By integrating the occupied ($W_+$) and unoccupied ($W_-$) spectral weights, we quantify the electron-hole asymmetry by calculating an asymmetry parameter (AP) as AP = ($W_+ - W_-)/(W_+ + W_-)$, which presents a systematic doping dependence and changes in its sign from n- to p-SLCO (top panel of fig. S10B). As plotted in fig. S10C is the $x$-dependent pseudogap magnitude $\Delta_p$, varying from ~ 28 meV in the
underdoped samples to ~ 11 meV in the near-optimally doped samples (x = 0.100). Our findings imply a common origin of the pseudogap phenomenology in electron and hole-doped cuprates. Despite the previous reports of electron-hole asymmetry in hole-doped cuprates (5, 11, 31), its verification in electron-doped ones as well as the above revealed dichotomy between n-SLCO and p-SLCO are totally new. These unusual and systematic results impose several constraints on nature of IGS as well as the extraordinary low-lying physics in cuprate superconductors.
Fig. S1. Kiessig fringes in a typical SLCO/SrTiO$_3$ hybrid structure. The La doping level is $x = 0.10$. The sharp and well-defined satellite peaks, from which we estimate the film thickness to be ~ 60 unit cells, are found to surround the main (002) Bragg peak and justify the good crystallinity of MBE-grown SLCO films.
Fig. S2. Hall measurements. (A-C) Transverse Hall resistivity $\rho_{xy}$ for SLCO films with the La doping level $x = 0.097$, 0.153, and 0.194. Gray lines designate the linear fits to data. (D) Calculated Hall coefficient ($R_H = \rho_{xy}/B$) versus temperature, showing the evolution of the carrier type and density $n_H$ across the critical La doping of $x \sim 0.104 - 0.132$. 
Fig. S3. HAADF-STEM of p-SLCO/SrTiO$_3$ hybrid structure (x = 0.167). (A-C) The images are acquired with the electron beam parallel to the [100], [010] and [11$ar{1}$0] directions, respectively. The horizontal dashes mark the interfaces of SLCO/SrTiO$_3$. Colored arrows mark the alternate variations of Cu (red and green) and Sr (yellow and white) atomic columns in intensity and shape, while the horizontal dashes mark the interfaces of SLCO/SrTiO$_3$. The dumbbell-like columns hint at the distortion or displacement of Cu and Sr atoms, predominantly in the a-b plane. The white rectangles mark the unit cells.
Fig. S4. Spatial homogeneity and determination of Mott parameters. (A) STM topography (60 Å × 60 Å, V = -1.5 V, I = 10 pA) on n-SLCO with a doping level of \( x = 0.061 \). As compared to SNCO, the surface morphology of epitaxial SLCO films on SrTiO\(_3\) are corrugated probably due to the larger mismatch between them. (B) Point spectroscopy measured on the dark region of the inserted STM image (marked by the white dot). The atomically-resolved STM image was acquired on the outlined region of (A) with a different sample bias of -0.8 V. The unchanged Mott-Hubbard band structure, with CTB and UHB below and above \( E_F \) suggests the integrity of CuO\(_2\) planes, albeit corrugated. Because the emergent IGS around the onsets of CTB and UHB, we have performed the linear fits to each \( dI/dV \) data justly above and below the CTB and UHB (red dashes) to more accurately determine the onsets of CTB and UHB, which are defined as the two intersections below and above \( E_F \) (black and blue arrows), respectively. The same conventions are used throughout. (C) \( dI/dV \) spectra taken at equal separation along the white arrow in (A) illustrating how homogeneous the CTB (black triangles) and UHB (blue triangles) onsets are on the corrugated CuO\(_2\) planes of SLCO. The spectra were measured by stabilizing the setpoint \( V = -1.8 \) V and \( I = 100 \) pA. Red dashed lines indicate the linear fits to the electronic DOS justly below and above CTB/UHB. (D) Determined \( \Delta_{CT} \) (top panel), onset energies of UHB (middle panel) and CTB (bottom panel) as a function of the measured position \( d \) from bottom to top along the arrow. The error bars arise from the uncertainty of linear fits to the electronic DOS near the band edges for calculating the UHB and CTB onsets. We find little variation in the Mott parameters. The horizontal lines are guide for the eye.
Fig. S5. Spatially-averaged $\text{d}I/\text{d}V$ spectra of undoped and slightly doped SLCO films. For each spectrum, the tunneling junction is stabilized to the starting voltage from the negative side and $I = 100$ pA. Due to the poor electrostatic screening of measured samples, the STM tip induces appreciable band bending and pushes the CTB (marked by black triangles) and UHB (marked by blue triangles) away from $E_F$ (21), rendering it improbable to measure $\Delta_{CT}$ correctly. Note that the $E_F$ of undoped SLCO cuprates lies at the midgap energy $E_i$, as anticipated.
Fig. S6. Bandwidths of CTB and UHB. (A) Representative $dl/dV$ spectrum ($V = -1.8$ V, $I = 100$ pA) on $n$-SLCO ($x = 0.054$). For occupied and unoccupied states, the backgrounds (red dashes) are individually extracted from an exponential fit to the data (empty circles) beyond the energy range of CTB and UHB. (B) Normalized DOS by subtracting the raw data by the background in the vicinity of CTB (green dots) and UHB (orange dots). The Gaussian fits to the normalized DOS lead to the bandwidths of 0.48 eV and 0.51 eV for CTB and UHB, respectively. (C and D) Representative $dl/dV$ spectrum ($V = 1.8$ V, $I = 100$ pA) on $p$-SLCO ($x = 0.206$) and the same data analysis as conducted for $n$-SLCO. The bandwidths of 0.49 eV and 0.45 eV are obtained for CTB and UHB. (E) Averaged bandwidths of CTB (green squares) and UHB (orange squares) as a function of La content $x$. The errors indicate the standard deviations from multi $dl/dV$ measurements (> 30 data points) over various regions.
Fig. S7. Structural characterization of SNCO epitaxial films. (A) XRD pattern of Sr$_{0.92}$Nd$_{0.08}$CuO$_2$ films acquired using the same monochromatic Cu K$_{\alpha 1}$ radiation with a wavelength of 1.5406 Å. The black and blue diffraction peaks originate from the SrTiO$_3$ substrate and SNCO films, respectively. The c-axis lattice constant is estimated to be $c \approx 3.43$ Å. (B) Kiessig fringes around the main (002) Bragg peak in the SNCO/SrTiO$_3$ hybrid structure. Based on the satellite peaks around, we calculate the film thickness to be $\sim 13$ unit cells.
Fig. S8. Screening of ionized defects in SNCO. (A and B) Dependence of $\Delta_{\text{CT}}$ (top panels), onset energies of UHB (middle panels) and CTB (bottom panels) on the lateral distance $d$ from the centers of single Nd$_{\text{Sr}}$ donor and O$_{\text{A}}$ acceptor, respectively. The errors indicate the uncertainty of linear fits to the electronic DOS near the band edges for calculating the UHB and CTB onsets. The two horizontal lines in the top panels are guide for the eye. (C and D) Lateral dependence of CTB onsets and UHB spectral weights around $V_{\text{Cu}}$, respectively. The error bars in (D) indicate the statistical standard derivation of UHB spectral weights obtained for different integration intervals of electronic DOS around UHB.
Fig. S9. Spatial phase separation. (A) STM topographies on epitaxial SLCO films with varying doping level $x = 0.054$ (80 Å × 80 Å, $V = -1.5$ V, $I = 10$ pA), 0.076 (50 Å × 50 Å, $V = 1.0$ V, $I = 30$ pA), 0.100 (60 Å × 60 Å, $V = 0.3$ V, $I = 10$ pA), 0.132 (100 Å × 100 Å, $V = -0.5$ V, $I = 20$ pA), 0.167 (160 Å × 160 Å, $V = 0.6$ V, $I = 10$ pA), 0.206 (80 Å × 80 Å, $V = -0.2$ V, $I = 30$ pA) from left to right. The cyan peripheries separate two distinct regions with pseudogap-like spectra in (B) (bright regions) and featureless dI/dV spectra in (C) (dark regions), while the white dots indicate the positions where the dI/dV spectra in (B) ($x = 0.054$ and 0.076) were measured. (B) Doping-
dependent $dI/dV$ spectra on the pseudogap regions with relatively high IGS. Note that the pseudogap-like electronic DOS depletion around $E_F$ is superimposed on a sloping background. (C) Spatial dependence of $dI/dV$ spectra acquired in regions with relatively low IGS. Albeit no pseudogap, the electron-hole asymmetry of IGS remains and changes in sign between $n$-SLCO and $p$-SLCO cuprates. The spectra have been vertically shifted for clarity of display. Setpoint: $V = 0.1$ V, $I = 200$ pA.
**Fig. S10. The pseudogap state.** (A) Spatially averaged $dl/dV$ spectra on pseudogap regions versus the La doping level $x$. As usual, we measured the pseudogap magnitude $\Delta_p$ to be half of energy separation between the two coherence peaks or kinks (marked by colored triangles). Note that all pseudogaps are superimposed on a sloped background and the slope changes in sign between $n$-SLCO and $p$-SLCO. Setpoint: $V = 100$ mV, $I = 200$ pA. (B) Asymmetry parameter AP (top panel) and $\Delta_p$ (bottom panel) plotted as a function of $x$. In $n$-SLCO, the unoccupied states are more prominent than the occupied states and thus the AP is negative, but in $p$-SLCO it is opposite. This illustrates a dichotomy between $n$-SLCO and $p$-SLCO cuprates.