Resolving Chemically Driven Charge Ordering in Infinite Layer Nickelates with Multislice Electron Ptychography and 4D-STEM

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Recently realized superconductivity in infinite-layer nickelates has opened a new avenue to explore correlated high-temperature superconductors and their competing phases [1,2]. While nickelates share a $3d^9$ electron configuration and crystal structure with the cuprates, there are significant differences in critical temperature and competing ground states [3]. In the cuprates, superconductivity competes with symmetry-breaking charge density wave phases at low temperatures, but in the nickelates whether such symmetry-breaking electronic order exists remains unclear. Experimental signatures of charge order in infinite-layer nickelates presumed to arise from an intrinsic electron correlation-driven charge density wave [4,5] have recently been attributed in some samples to ordering of excess oxygen present in the materials [6,7]. Because of the substantial interplay between superconductivity and charge order found in other high-temperature superconductors, clarifying the nature of charge order in the nickelates is critical to understanding superconductivity in this system.

To investigate the nature of charge order in infinite layer nickelate thin films, we leverage a suite of scanning transmission electron microscopy (STEM) techniques to characterize a series of capped $NdNiO_{2+x}$ thin films as a function of excess oxygen concentration. In particular, we study the crystalline structure of the films with atomic resolution to search for symmetry-breaking distortions and possible correlation to the presence of ordered excess oxygen. Conventional methods for characterizing oxygen in real space such as annular bright-field (ABF) and integrated differential phase contrast (iDPC) imaging suffer from limited spatial resolution and artifacts from mistilt and incoherency in the projection direction leading to unreliable mapping of oxygen occupancy [8,9]. In finely tuned material systems such as the partially-reduced nickelates studied here, phase coexistence makes it particularly difficult to avoid such artifacts in ABF and iDPC. Here, we use multi-slice electron ptychography [10] to overcome these challenges, properly account for multiple scattering, and achieve strong interpretable contrast, high lateral resolution, and even recover depth information, resolving the 3D phase distribution. Insights of the atomic structure of heavy and light atoms obtained from electron ptychography, we see the clear presence of oxygen ordering in Nd-based infinite-layer nickelate thin films correlating with other signatures of charge order. We quantitatively map (described in [11]) the changes in bond length and cation lattice associated with the charge ordering. Along with the atomic resolution information gained from distortion mapping of ptychographic reconstruction, mesoscale visualization of distribution of charge ordering domains through nano-diffraction allows us to understand the nature of charge order in nickelates.

A ptychographic reconstruction reveals the presence of oxygen-occupying sites which are nominally vacant in the infinite layer structure with a $3a_0$ periodicity - a period similar to that of previously reported charge order (Fig 1a). Oxygen octahedral rotations in this region resemble the perovskite parent structure. Displacements of Nd and Ni sites are mapped (Fig 1 d,e) with the technique described in [11]. Areas with no sign of the charge order resemble the infinite layer structure (Fig 1c) with no Nd and Ni displacements, indicating the displacements arise solely from the excess-oxygen ordering. Superlattice peaks arising from these displacements are used to visualize the excess-oxygen ordering using electron nano-diffraction on the mesoscale. As observed in Fig 2a the ordering is not uniform across the film but exists in dispersed domains. Areas outside of the ordered excess-oxygen domains match the infinite layer structure with no superlattice peaks observed (Fig 2c), in agreement with the ptychography images. This suggests that the signatures of charge order in $NdNiO_{2+x}$ are due to the presence of excess oxygen rather than an intrinsic electron-correlation driven density wave. This work demonstrates the capability for highly localized and sensitive characterization with electron ptychography correlated with mesoscale mapping with nano-diffraction to disentangle the complex phases and nanoscale structures arising in highly-correlated systems such as nickelates [12].

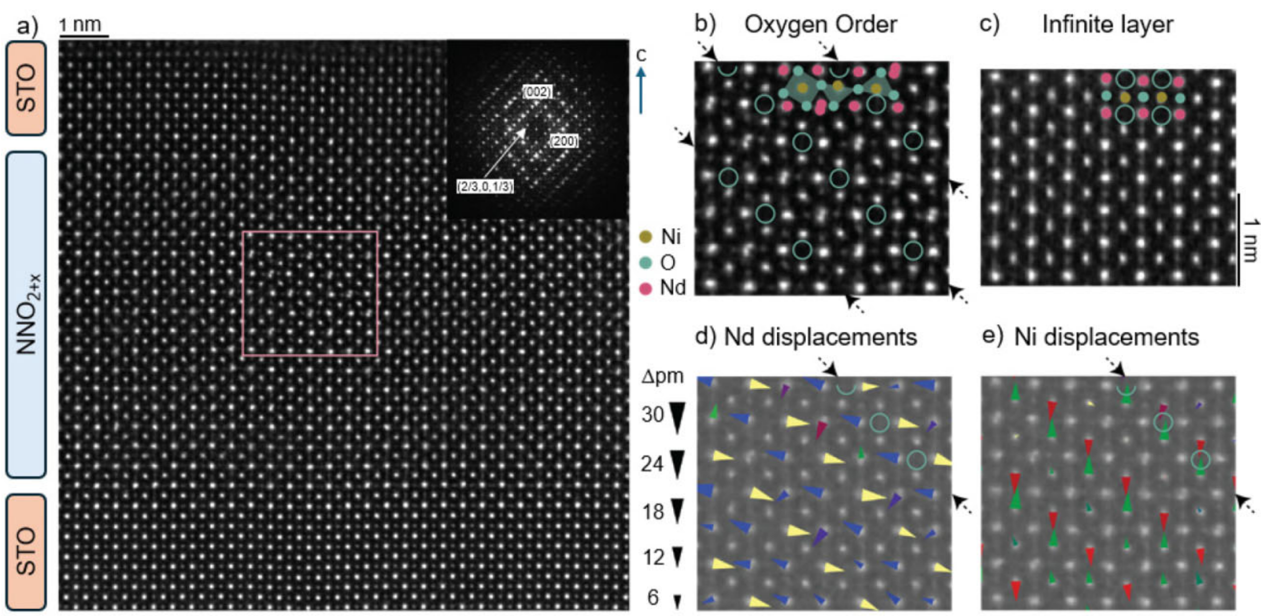

Figure 1. (a) Ptychographic reconstruction of ordered oxygen area in $NdNiO_{2+x}$ with inset showing the FFT of the image with $3a_0$ period superlattice peaks. Pink square indicates the area enlarged in (b). Clear absence of oxygen atoms is observed at sites highlighted by green hollow circles ordering with $3a_0$ periodicity. (c) Ptychographic reconstruction of a different area from the same film without superlattice peaks, which shows the infinite-layer structure. Displacement map of Nd (d) and Ni (e) distortions in (b) illustrating how the Nd and Ni cations displace away from and towards the oxygen vacancies.

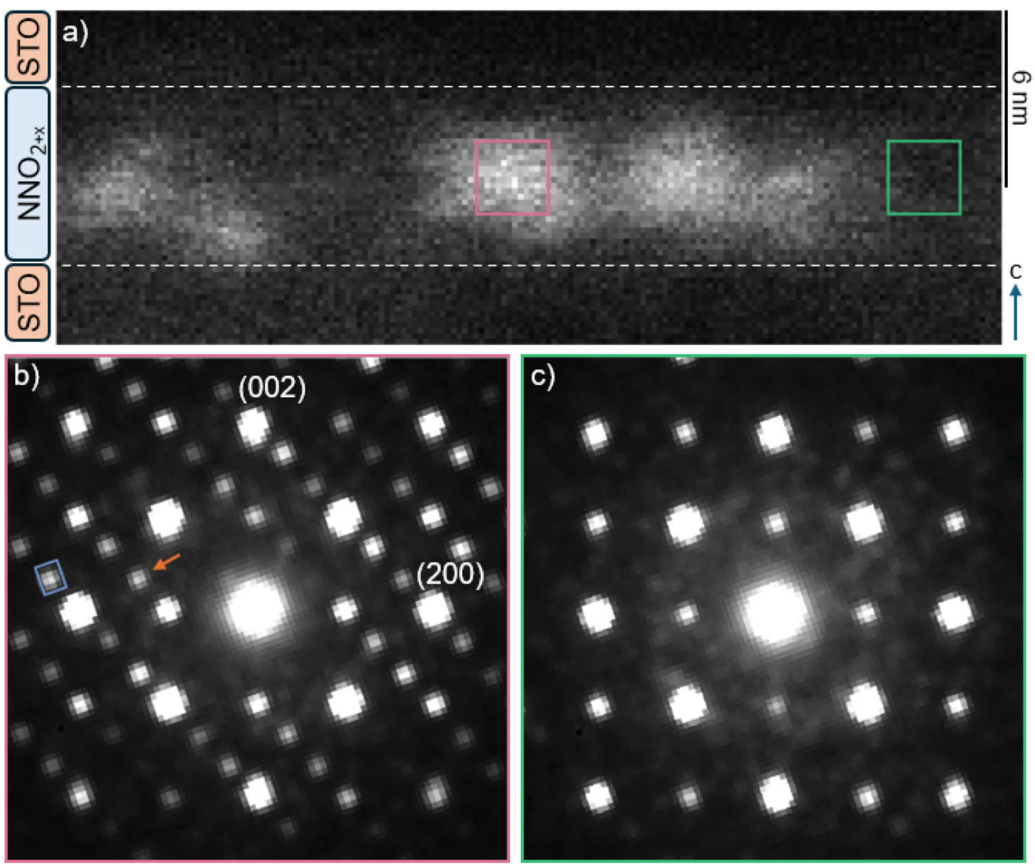

Figure 2. Darkfield Imaging of Oxygen Ordering by 4D-STEM (a) Map of oxygen ordering domains created by fourier filtering superlattice peak highlighted by blue square in (b). (b) Summed 4D-STEM dataset of area highlighted by pink square in (a) showing superlattice peaks (orange arrow) with $3a_0$ periodicity. (c) Summed 4D-STEM dataset of areas highlighted by green square in (a) with no observable superlattice peaks.

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