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Structural and Magnetic Properties of Nanosized $LiCoO_2$ Surfaces

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$LiCoO_2$ (LCO) nano particles have attracted extensive scientific interest in the recent decade owing to the great potential to increase the charge/discharge-rate capacity when used as the cathode material for Li-ion batteries. [1] It has been demonstrated that the physical properties, including lattice parameters and magnetic susceptibility of the LCO nano particles significantly differs from those of the LCO bulk due to surface effects. [2] LCO nano platelets have been predicted to consist of several low-index surfaces, including the (001), (104), and (012) surfaces, [3] as shown in Figure 1(a). Furthermore, electronic spin state transition is found to occur at the LCO surfaces, where intermediate spin Co^{3+} ions are present at (104) surfaces. [4] However, the experimental demonstration of the LCO surface fine structure and the physical understanding of surface magnetism the are still elusive. In this work, we performed a combined experiment-theory study, using scanning transmission electron microscopy (STEM), electron energy-loss spectroscopy (EELS), X-ray absorption spectroscopy (XAS) and density functional theory (DFT) modeling, to explore the surface properties of LCO nano platelets.

The high-angle annular dark-field (HAADF), low-angle annular dark-field (LAADF) and annular bright-field (ABF) images for the LCO nano platelets, as shown in Figure 1(b)-(d), are obtained using the aberration-corrected JEOL JEM-ARM200CF microscope operating at an acceleration voltage of 200 kV. The structures of (001) and (104) facets can be directly observed from the atomic-resolution HAADF and ABF images along the [010] zone axis. We note that the edges of the nano platelets are atomically abrupt without significant structural reconstruction compared with the bulk structure. The O *K*-edge is measured using both EELS and XAS methods. As shown in Figure 1(e) and (f), the O *K*-edge prepeak shows a single peak at 531.6 eV in EELS, while two split peaks at 530.8 eV and 532.6 eV in the XAS, which suggests that the electronic structure of LCO bulk is significantly different from that of the surface. The splitting of the O *K*-edge prepeak has not been reported in previous literature to the best of our knowledge. First-principles DFT modeling is carried out using the generalized gradient approximation with the Hubbard *U* correction method to understand the surface properties of LCO nanoplates. A slab model with two symmetric surfaces separated by a vacuum is used to simulate the LCO (001), (104) and (012) surfaces.

In this presentation, we combine DFT modeling with EELS and XAS and show that the splitting of O *K*-edge prepeak is due to the Co^{3+} spin state transition from low spin (LS) to intermediate spin (IS) states at different surfaces. The results from our DFT calculations are shown in Figure 2. We will further discuss how the orbital-projected O 2*p* states at the (104) surface contribute towards the peak splitting as the results of the Co 3*d*-O 2*p* hybridized states with in-plane IS Co-O bonding which has a strong two-dimensional character. The splitting behavior of O *K*-edge prepeak can only be observed from LCO nano particles which have large surface areas. Furthermore, the intensity of the two split peaks is found to be directly related to the density of surface Co^{3+} IS and LS states. Thus, the change of the relative intensity ratio of the split O *K*-edge prepeaks is capable of reflecting the change of surface Co^{3+} IS/LS ratio. [5]

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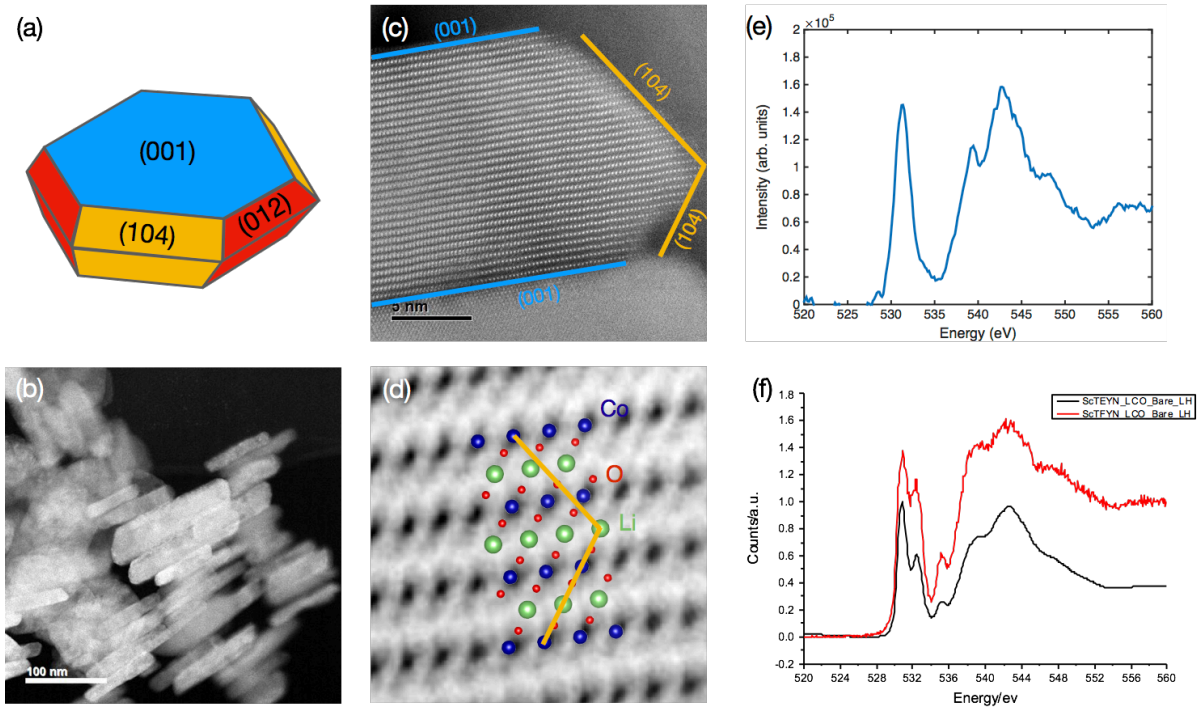

Figure 1. (a) Schematic of the LCO nano platelets with (001), (104) and (012) facets. (b) LAADF image showing the stacked LCO nano platelets. (c) Atomic-resolution HAADF image along [010] showing the (001) and (104) edges. (d) Atomic-resolution ABF image along [010] with DFT-optimized structural model as inset. (e) EELS O *K*-edge spectrum. (f) XAS O *K*-edge spectra in TEY and TFY modes.

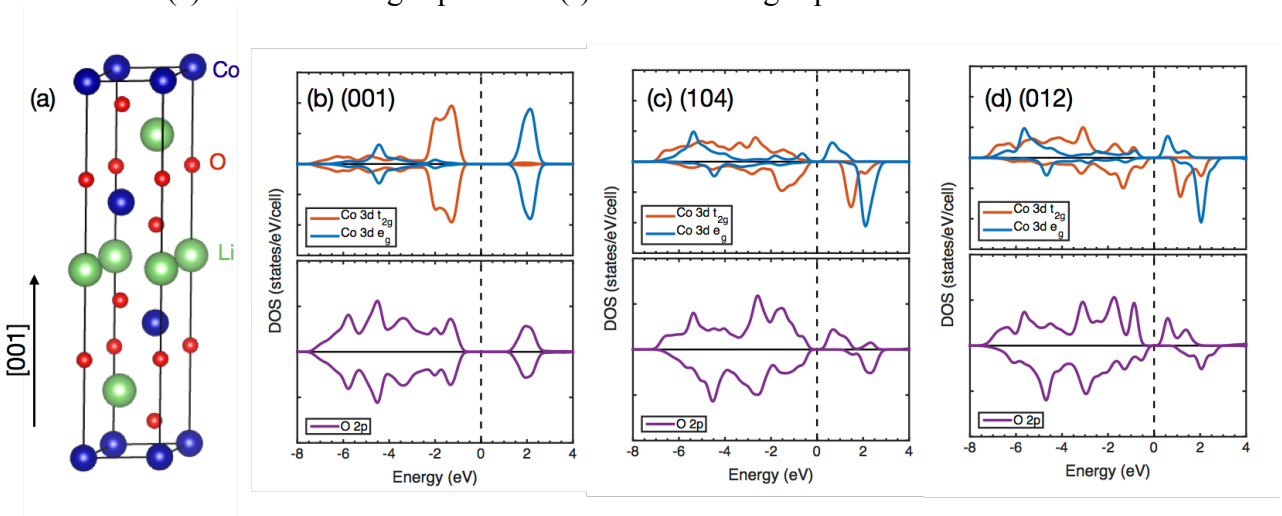

Figure 2. (a) DFT structural model for LCO unit cell. (b)-(d) Spin-resolved PDOS on the surface Co 3*d* and O 2*p* orbitals for (001), (104) and (012) surfaces.

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