ABSTRACT

A Chemical Approach to Understanding Oxide Surface Structure and Reactivity

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Transmission electron microscopy and diffraction are powerful tools for solving complex structural problems. They complement other analytical techniques, such as x-ray diffraction, elucidating problems which cannot be solved by other techniques. One area where they are of particularly great value is in the determination of surface structures. The research presented herein uses electron microscopy and diffraction as the primary experimental techniques in the development of a chemistry of surface structures.

High-resolution electron microscopy revealed that the $La_4Cu_3MoO_{12}$ structure has turbostratic disorder and a lower symmetry space group (*Pm*) than was previously found. The refinement of the x-ray data was significantly improved by using a disordered model and the *Pm* space group. A bond valence analysis confirmed that the disordered structure is the superior model.

Strontium titanate, $SrTiO_3$, single crystal surfaces were examined principally via transmission electron diffraction. A homologous series with intergrowths was discovered on the (110) surface of strontium titanate, marking the first time that these important concepts of solid state chemistry have been found at the surface. Atmospheric adsorbates, such as H_2O and CO_2, were found to help to stabilize undercoordinated surface structures on the (100) surface. It was

shown that chemical bonding, bond valence, atomic coordination, and stoichiometry greatly influence the development of surface structures. Additionally, such chemistry based analysis was demonstrated to be able to predict surface structure stability and reactivity.

Application of a modified Wulff construction to the observed shape of strontium titanate nanocuboids revealed that the surface structure and particle stoichiometry are interlinked, with control over one allowing equally precise control over the other. Platinum nanoparticles on the strontium titanate nanocuboids were shown via high resolution electron microscopy to have cube-on-cube epitaxy, with the shape of the platinum nanoparticles governed by the Winterbottom construction. Precise modification of the support surface will therefore allow engineering of supported metal particles with precise control over which facets are exposed. These results suggest that control over the support surface chemistry can be used to engineer thermodynamically stable, face selective catalysts.

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