

Thursday Morning, October 22, 2015

Scanning Probe Microscopy Focus Topic
Room: 212A - Session SP+AS+NS+SS-ThM

Probing Chemical Reactions at the Nanoscale

Moderator: Stephen Nonnenmann, University of Massachusetts - Amherst, Shengyong Qin, University of Science and Technology of China

8:40am **SP+AS+NS+SS-ThM3 Adsorption of Trimethyl Acetic Acid on (1x2) Reconstructed TiO₂(110)**, *Kenneth Park, K. Zhu, Y. Xia, Z. Zhang*, Baylor University

The adsorption of trimethyl acetic acid on (1x2) reconstructed TiO₂(110) is investigated using scanning tunneling microscopy (STM) with the same area analysis. After de-protonation, trimethyl acetate (TMA) molecules preferentially adsorb in the troughs between two adjacent 1x2 strands. The nearest neighbor distance between TMA molecules is about 5.9 Å, twice the lattice constant along [001], corresponding to the bridging bidentate configuration over two 5-coordinated Ti⁴⁺ sites. With increasing coverage, they form linear chains, separated by (1x2) strands leading up to the nominal saturation coverage of 0.25 ML. Upon further adsorption, the second-layer of TMA molecules start clustering on top of 1x2 strands. The coverage-dependent TMA adsorption structures on (1x2) reconstructed TiO₂(110) will be compared and discussed with the reported TMA adsorption on (1x1) TiO₂(110), and relative reactivity of TMA with other defect sites including cross-links will be presented.

9:00am **SP+AS+NS+SS-ThM4 Anticorrelation between Surface and Subsurface Point-Defects and Influence on Redox Chemistry at TiO₂(110)**, *Igor Lyubinetsky, Y. Yoon, Y. Du*, Pacific Northwest National Laboratory, *J.C. Garcia*, Worcester Polytechnic Institute, *Z. Zhu, Z.-T. Wang, N.G. Petrik, G.A. Kimmel, Z. Dohnalek, M.A. Henderson, R. Rousseau*, Pacific Northwest National Laboratory, *N.A. Deskins*, Worcester Polytechnic Institute

The atoms at the surface that constitute reactive sites clearly govern surface chemistry. But subsurface atoms, particularly substitutional and/or interstitial defects, can also influence surface chemistry, though a detailed understanding is still emerging. Here we report the interplay and relative impact of surface vs. subsurface defects on the surface chemistry of rutile TiO₂, a prototypical metal oxide. Importantly, it contains both surface and subsurface intrinsic point-defects in the reduced state (along with residual extrinsic defects). Our scanning tunneling microscopy results show that O vacancies (V_O's), the dominant surface defects, are virtually absent in the vicinity of positively-charged subsurface point-defects. Such anticorrelation of defects is consistent with density functional theory (DFT) calculations of the impact of subsurface defect proximity on V_O formation energy, which narrows down the possible candidates to certain interstitial defects, of both intrinsic and extrinsic nature. To monitor the influence of such (electron-donor type) defects on surface redox chemistry, a test reaction of the electron-mediated dissociative adsorption of O₂ is employed, which is observed to be suppressed around these defects. DFT results attribute this to a perceived absence of the intrinsic (Ti) (and likely extrinsic) interstitials in the nearest subsurface layer beneath "inhibited" areas, while the underlying energetic driver is largely repulsive electrostatics. Finally, we postulate that the entire subsurface region up to several atomic layers deep could be voided of any charged point-defects, whereas such defects are proposed to exist beyond the subsurface region. Subsequently, prevalent V_O's are largely responsible for both the surface/subsurface reduction and mediation of the redox chemistry at reduced TiO₂(110) surface. Overall, this work provides new fundamental insights into the relation between surface and subsurface defects. In a broader perspective, the uncovered effects may prove to be general for other reducible oxides, and thus have potential implications in such diverse research fields as environmental remediation or microelectronics.

9:20am **SP+AS+NS+SS-ThM5 Dissociation of Water on Oxygen Pre-Covered Cu(110) Observed with Scanning Tunneling Microscopy**, *Zongqiang Pang*, Lawrence Berkeley National Laboratory (LBNL)

The dissociation of water on the oxygen pre-covered Cu(110) surface has been studied with Scanning Tunneling Microscopy (STM). At low temperature (77K), water reacts with pre-covered oxygen to produce hydrogen atoms and hydroxyl groups. Non-dissociated water molecules and hydroxyl groups combine to form a hexagonal network on the top of Cu(110) where water donates one hydrogen to the hydroxyl, while uncoordinated hydroxyls bind to the second layer intact water molecules. Following excitation by tunneling electron or by heat, the water molecules

in the hexagonal network gradually dissociate. The oxygen atoms involved in the reaction of water dissociation return to its original position, leaving ordered Cu-O and hydroxyl dimer chains on the Cu(110) surface which both align along <001> direction. Our results demonstrate that the oxygen atoms pre-adsorbed on the Cu(110) surface lower the energy barrier for water dissociation on the Cu(110) surface.

9:40am **SP+AS+NS+SS-ThM6 Probing Local Electrochemical Activity within Yttria-Stabilized-Zirconia via In Situ High-Temperature Atomic Force Microscopy**, *Jiaxin Zhu*, University of Massachusetts - Amherst, *C. Perez, T. Oh, R. Kungas, J. Vohs, D. Bonnell*, University of Pennsylvania, *S.S. Nonnenmann*, University of Massachusetts - Amherst

Considerable interest in understanding interfacial phenomena occurring across nanostructured solid oxide fuel cell (SOFC) membrane electrode assemblies has increased demand for *in situ* characterization techniques with higher resolution. We briefly outline recent advancements in atomic force microscopy (AFM) instrumentation and sub-systems in realizing real time imaging at high temperatures and ambient pressures, and the use of these *in situ*, multi-stimuli probes in collecting local information related to physical and fundamental processes. Here we demonstrate direct probing of local surface potential gradients related to the ionic conductivity of yttria-stabilized zirconia (YSZ) within symmetric SOFCs under intermediate operating temperatures (500 °C – 600 °C) via variable temperature scanning surface potential microscopy (VT-SSPM). The conductivity values obtained at different temperatures are then used to estimate the activation energy. These locally collected conductivity and activation energy values are subsequently compared to macroscopic electrochemical impedance results and bulk literature values, thus supporting the validity of the approach.

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