Atomic-scale Chemical Imaging via Combination of Scanning Tunneling and Electron Energy Loss Spectroscopies

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Purpose

- Atomic-level, mechanistic understanding of catalytically important systems (water and CO_2 on $RuO_2(110)$ and $TiO_2(110)$)
- Develop atomically resolved chemical imaging platform: low-temperature scanning tunneling microscope (LT STM) with in-situ molecular beam and ex-situ electron spectroscopies

Expected Outcomes

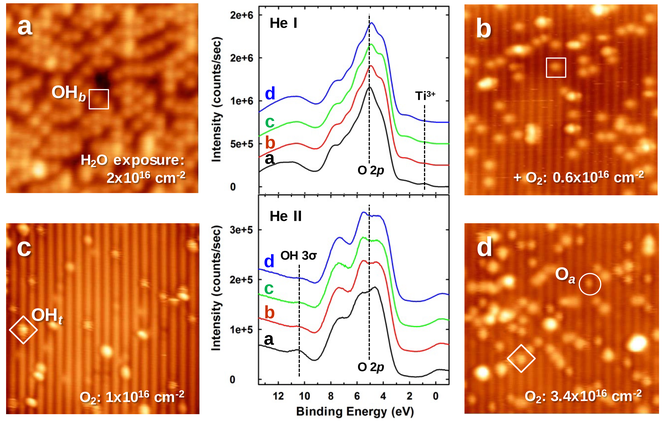
- Multimodal spectroscopic capability for chemically specific, surface-sensitive imaging at atomic/molecular level
- Superior spatial resolution compared to tip-enhanced Raman

Key Successes

- Completed and successfully tested molecular beam device in-situ coupled with LT STM for tip functionalization

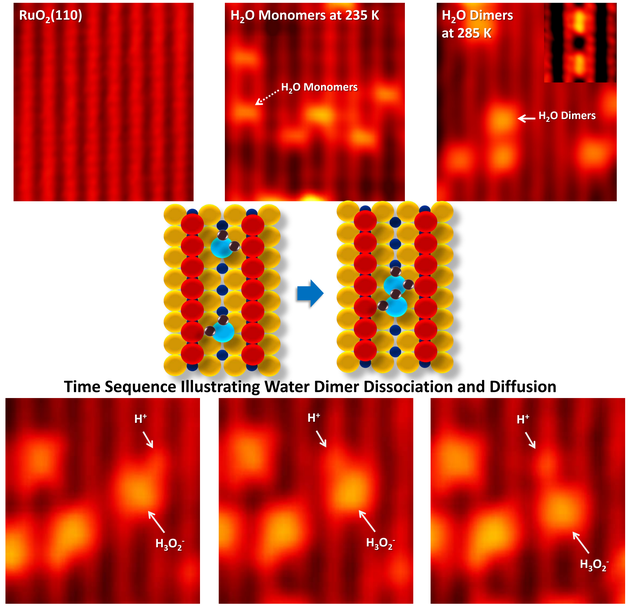
Research Accomplishments

Redox State of O-Vacancy-Free $TiO_2(110)$ Surface



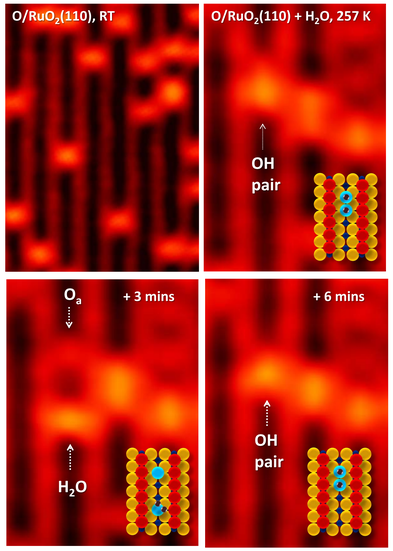
- Chemical identity of adsorbed species inferred from known reagents
- UV photoelectron spectra provide ensemble-averaging information on surface electronic structure (valence band, defect gap states, and adsorbates)
- First inelastic electron tunneling spectroscopy (IETS) experiments, supplying single molecule-specific vibrational signatures, are forthcoming

Coverage-Dependent Water Structures on $RuO_2(110)$



- Detailed experiments reveal deprotonated H_2O dimer ($H_3O_2^-$ + H^+) as a most stable configuration
- Monomers and molecularly bound dimers also observed at low temperatures
- Range of well-defined species for IETS spectroscopic studies

Reactions of Water with Oxygen Atoms on $RuO_2(110)$



- Ru-bound hydroxyls prepared by reacting water monomers with Ru-bound oxygen atoms
- Additional types of water-based surface species for IETS studies can be prepared.

Next Steps

- Measure inelastic electron tunneling spectra for well-characterized H_2O- and CO_2-derived surface species on $RuO_2(110)$ and compare against high-resolution electron energy-loss spectra

Publications

- Wang Z et al. 2012. *Physical Review Letters* 109:266103
- Henderson MA and I Lyubinetsky. 2013. *Chemical Reviews* 113:4428
- Lin X et al. 2013. *Physical Chemistry Chemical Physics* 15:6190
- Henderson MA et al. 2013. *Journal of Physical Chemistry C* 117:5774