

## Surface Science

Room: 201 A - Session SS+EN-ThM

## Photocatalysis and Photochemistry at Surfaces

Moderator: G.A. Kimmel, Pacific Northwest National Laboratory

8:00am **SS+EN-ThM1 Hinderer Influence of Oxygen Vacancies for Photoactivity on TiO<sub>2</sub>(110)**, *I. Lyubinetsky, Z.T. Wang*, Pacific Northwest National Laboratory, *N.A. Deskins*, Worcester Polytechnic Institute, *M.A. Henderson*, Pacific Northwest National Laboratory

In photoinduced processes, surface point-defects are expected to act as charge trapping and/or recombination centers. However, the direct impact of surface defects on photoreactivity is not well explored. We present the first observation of a suppressing effect of oxygen vacancy ( $V_O$ ) defects on photoreactivity of TiO<sub>2</sub>(110). Direct scanning tunneling microscopy imaging reveal a pronounced site-selectivity in the hole-mediated photooxidation of trimethyl acetate (TMA) on TiO<sub>2</sub>(110) upon ultra-violet light irradiation, wherein the reaction readily occurs at regular Ti sites but is completely inhibited at  $V_O$  defects. Utilizing electron energy loss spectroscopy and density functional theory, we show that the lack of reactivity of TMA groups adsorbed at  $V_O$ 's cannot be attributed to either a less active adsorption conformation or electron transfer from the  $V_O$  defect. Instead, we propose that the excess unpaired electrons associated with the  $V_O$  promptly recombine with photoexcited holes approaching the surface, effectively 'screening' TMA species at  $V_O$  site. We also show that this screening effect is spatially short-ranged, being predominately localized at the  $V_O$ , and only mildly affecting TMA's at adjacent Ti sites. The direct impact of O vacancies on TMA photoreactivity over TiO<sub>2</sub>(110) is expected to have similar implications for other hole-mediated (e.g., photooxidation) reactions in which adsorption at or near electronic point-defects is possible. Furthermore, the localized influence of these defects on hole-mediated chemistry offers opportunities for additional study of site-selective photocatalysis on TiO<sub>2</sub>. The presented results also demonstrate that structure-reactivity relationships, a customary subject in heterogeneous catalysis, are clearly relevant to photocatalysis.

8:20am **SS+EN-ThM2 Anisotropic Photochemical Reactivity of Rutile (110)**, *A. Song, D. Jing, M.A. Hines*, Cornell University

The surface chemistry of nanocrystalline titanium dioxide has garnered a tremendous amount of attention over the past decade due to a number of high-profile applications, including dye-sensitized solar cells and photoactivated self-cleaning or environmentally-remediating surfaces. Since most surface science investigations study pristine surfaces in ultrahigh vacuum conditions, little is known about the photoreactivity of surfaces in aqueous solutions. In particular, do certain sites on the surface dominate reactivity or are all sites equally reactive? To gain insight into the site specificity (or chemical anisotropy) of the reactions, we have used *ex situ* scanning tunneling microscopy to investigate the reaction of aqueous solutions of H<sub>2</sub>O<sub>2</sub> with rutile (110). Contrary to naïve expectation, above band gap radiation appears to suppress certain chemical reactions while also increasing reaction anisotropy. This finding suggests that some sites on the surface are more photoreactive than others. A mechanism that explains this anisotropy will be proposed.

9:20am **SS+EN-ThM5 Energy Transfer and Photostimulated Desorption of Atoms and Molecules Co-adsorbed with Oxygen on TiO<sub>2</sub>(110) Surface**, *N.G. Petrik, G.A. Kimmel*, Pacific Northwest National Laboratory

Titanium dioxide is a widely used photocatalyst. However, fundamental aspects of the photochemistry, including the role of molecular oxygen in photooxidation reactions, are still actively debated. Here, we use weakly bound (i.e. physisorbed) atoms and molecules, such as Ar, Kr, Xe, CO<sub>2</sub> and N<sub>2</sub>, to probe the photochemical interactions of O<sub>2</sub> on rutile TiO<sub>2</sub>(110). UV irradiation of chemisorbed O<sub>2</sub> along with the physisorbed probe species lead to photon-stimulated desorption (PSD) of the probe species. Without O<sub>2</sub>, the PSD yields of the probe species are very low or not observable. However, the Ar, Kr and N<sub>2</sub> PSD yields increase with increasing coverage of chemisorbed O<sub>2</sub>. No PSD was observed for CO<sub>2</sub>, and the PSD yield for Xe is very low compared to the other probe atoms or molecules. The angular distribution of the photo-desorbing Kr, which is broad and cosine, is quite different from the O<sub>2</sub> PSD angular distribution, which is sharply peaked along the surface normal. We propose a mechanism for the observed phenomena, where the chemisorbed O<sub>2</sub> serve as photoactive centers, excited via electronic excitations (electrons and/or holes) created in the TiO<sub>2</sub>

substrate by UV photon irradiation. The photo-excited O<sub>2</sub> may transfer its energy to neighboring co-adsorbed atoms or molecule resulting in their desorption. Simple momentum transfer considerations suggest that heavier adsorbates (like Xe) and adsorbates with higher binding energy (like CO<sub>2</sub>) would desorb less efficiently according to the proposed mechanism.

9:40am **SS+EN-ThM6 Adsorption and Photo-induced Decomposition of Formate on Rutile TiO<sub>2</sub> (110)**, *A. Mattsson, S. Hu, K. Hermansson, L. Österlund*, Uppsala University, Sweden

Adsorption of formic acid on rutile TiO<sub>2</sub> (110) were studied with reflection absorption infrared spectroscopy (RAIRS) in UHV with both s- and p-polarized IR light, incident along either the <001> or <1-10> direction. Experiments were conducted on surfaces prepared with different pre-treatments to obtain stoichiometric (s-TiO<sub>2</sub>), oxidized (o-TiO<sub>2</sub>) and reduced (r-TiO<sub>2</sub>) surfaces. Experiments were compared with density functional theory (DFT) calculations as implemented in the Vienna ab initio simulation package (VASP).

With p-polarized light, transmission and absorption peaks are observed due to the symmetric and asymmetric O-C-O stretch and C-H wagging modes in formate bonded to the Ti-atoms between the bridging oxygen rows in the <001> direction, in agreement with the measurements made by Hayden and co-workers.[1] This orientation of the formate molecule is dominant on for all surface preparations studied here. Employing s-polarized light reveals that the C-H wagging occurs in the plane of the molecule, since it is only seen with s-polarized light incident in the <1-10> direction. In the earlier work by Hayden, weak absorption peaks were observed with p-polarized light incident in the <1-10> direction, and attributed to a minority specie, oriented perpendicular to the majority specie, and bonded to bridging oxygen vacancies. This interpretation is at variance with our results for s-polarized light, and furthermore an equally weak band is seen regardless of the surface preparation. We attribute this to rapid hydroxylation of the bridging oxygen vacancies in good agreement with recent STM studies, which show that bridging oxygen vacancies become hydroxylated within a few minutes at pressures of 3x10<sup>-10</sup> mbar.[2] DFT calculations support the above assignments, and in particular show that the minority species inferred from RAIRS is due to formate bonded to OH groups and not to bridging oxygen vacancies. We discuss the implications of our results for the photo-induced decomposition of formic acid on TiO<sub>2</sub>(110).

[1] B.E. Hayden, A. King, M.A. Newton, Journal of Physical Chemistry B **103** (1999) 203-208.

[2] S. Wendt, *et. Al.* Surf. Science **598** (2005) 226-245.

10:40am **SS+EN-ThM9 TiO<sub>2</sub> Nanoparticle Arrays Functionalized with Pt Photodeposition: Studies Using X-ray Spectroscopies under *In Situ* Heating and Hydrogen Annealing**, *Y. Liu, J. Taing, H. Bluhm, Z. Liu, Lawrence Berkeley National Laboratory, M. Veenendaal, Argonne National Laboratory, T. Devereaux, SLAC National Accelerator Laboratory, J.C. Hemminger, University of California, Irvine*

Using ambient pressure x-ray spectroscopies, we report the electronic and surface structures of TiO<sub>2</sub> nanoparticle arrays with and without Pt photodeposition under *in-situ* heating and hydrogen annealing. X-ray absorption and transmission electron microscopies indicate that the TiO<sub>2</sub> nanoparticles are in the rutile phase, but the anatase phase also can exist after Pt photodeposition. Valence photoemission results demonstrate a band gap narrowing when Pt is loaded onto the surface of TiO<sub>2</sub> nanoparticles. Upon heating the samples, surface defects and oxygen vacancies are formed, which could prevent the recombination of electron-hole pairs. Heating also enhances the occupation of metallic Pt on top of the TiO<sub>2</sub>. In contrast, introducing hydrogen at high temperature would enhance the Pt<sup>+</sup> species related to the strong metal support interaction. The reduced band gap and the increased contact surface in the Pt-photodeposited TiO<sub>2</sub> nanostructures can potentially enhance the performance of these materials in solar absorption and photocatalysis applications.

Reference:

Taing, J.; Cheng, M. H.; Hemminger, J. C., Photodeposition of Ag or Pt onto TiO<sub>2</sub> Nanoparticles Decorated on Step Edges of HOPG. *ACS Nano* 2011, 5, 6325-6333.

Liu, Y.; Taing, J.; Chen, C.-C.; Sorini, A. P.; Cheng, M. H.; Margarella, A. M.; Bluhm, H.; Devereaux, T. P.; Hemminger, J. C., Narrowing of Band Gap in Thin Films and Linear Arrays of Ordered TiO<sub>2</sub> Nanoparticles, to be submitted to *ACS Nano*.

11:00am **SS+EN-ThM10 Carrier Dynamics on Oxide Surfaces Studied by Time-resolved Soft X-ray Photoelectron Spectroscopy**, *S. Yamamoto, R. Yukawa*, The University of Tokyo, Japan, *M. Emori*, Sophia University, Japan, *K. Ozawa*, Tokyo Institute of Technology, Japan, *M. Ogawa, K. Fujikawa, Sh. Yamamoto, R. Hobara, I. Matsuda*, The University of Tokyo, Japan

Photocatalytic reactions on semiconductor oxide surfaces can be divided into four processes: (i) photon absorption, (ii) electron-hole pair formation, (iii) transport of photo-excited carriers from bulk to surface, and (iv) surface redox reactions. It is important to understand the dynamics of photo-excited carriers in order to make more efficient photocatalysts. Despite of its importance, little is known about transient electronic structures of photo-excited semiconductor surfaces.

Photoelectron spectroscopy (PES) has been successful in providing direct access to electronic structures of materials with surface sensitivity. The extension of PES to time-domain, or time-resolved PES, is now realized by the use of brilliant short pulse (several tens ps) x-ray available at the state-of-the-art synchrotron radiation facilities [1]. This allows us to study transient electronic structures of materials.

In this talk we will introduce the newly developed time-resolved PES system at the high-brilliance soft x-ray beamline BL07LSU at SPring-8 [2]. In the time-resolved PES measurements, the transient electronic structures after optical excitation by fs-laser pump pulses are monitored by ps soft x-ray probe pulses. The time-resolved PES studies on the relaxation of surface photovoltage effect on oxide surfaces such as SrTiO<sub>3</sub>(001) and ZnO(0001) will be presented.

#### References

- [1] S. Yamamoto, I. Matsuda, J. Phys. Soc. Jpn., 82, 021003 (2013).
- [2] M. Ogawa, S. Yamamoto, Y. Kousa, F. Nakamura, R. Yukawa, A. Fukushima, A. Harasawa, H. Kondoh, Y. Tanaka, A. Kakizaki, I. Matsuda, Rev. Sci. Instrum., 83, 023109 (2012).

11:20am **SS+EN-ThM11 Atomic Scale Photochemistry with STM**, *A.X. Yu, S.W. Li, G. Czap, Y.N. Zhang, H.Y. He, R.Q. Wu, W. Ho*, University of California, Irvine

The STM has proven to be an invaluable tool for studying surface chemistry at the atomic and molecular scale, such as bond formation, bond breaking, and photo-catalysis. Here we present STM studies on photon-induced desorption of H<sub>2</sub> molecules from Au (110) surface. Upon laser irradiation, H<sub>2</sub> is found to desorb from Au surface. We attribute the desorption mechanism to excitation of molecular vibrational modes by photon-induced hot electrons. We also study the photo-induced desorption and reaction of CO and O<sub>2</sub> on Al<sub>2</sub>O<sub>3</sub> / NiAl (110) surface. We hope to have a better understanding of various mechanisms for photon mediated reactions and effects of plasmon modes in nearby nanoparticles on chemical reactions.

11:40am **SS+EN-ThM12 Atomic Structure and Catalytic Activity of Size-Selected MoS<sub>2</sub> Nanoclusters for Water Splitting**, *R.E. Palmer, M. Cuddy, K. Arkill, Z.W. Wang, N.V. Rees*, University of Birmingham, UK

The green production of hydrogen by photocatalytic splitting of water molecules requires the catalyst both to absorb solar photons and to supply excited carriers of the correct energy to split water. MoS<sub>2</sub> is a new and abundantly available candidate catalyst material with a layered structure in the bulk; it is believed that quantum confinement in MoS<sub>2</sub> nanoparticles will allow the band gap and energy levels to be tuned to maximize the efficiency of water splitting. Here we report the atomic structure of size-selected nanoparticles (clusters) of MoS<sub>2</sub>, generated by magnetron sputtering of a bulk target and condensation in helium gas, then size selection with a novel lateral time-of-flight mass filter [1] prior to deposition onto carbon supports. X-Ray Photoelectron Spectroscopy (XPS) of cluster ensembles confirms that approximately stoichiometric compound clusters, with average formula MoS<sub>1.95</sub>, are produced (although we find they are somewhat sensitive to oxygen).

Atomic-scale imaging of the deposited MoS<sub>2</sub> clusters by aberration-corrected Scanning Transmission Electron Microscopy (STEM) [2] of the MoS<sub>2</sub> clusters shows layered nanoparticle structures (as opposed to e.g. fullerene structures), presenting ordered hexagonal arrays of Mo atoms. The cluster growth is remarkably anisotropic, such that as cluster size increases from 150-1000 MoS<sub>2</sub> units (always mass selected) the lateral diameter of the clusters increases but the mean vertical height (2.3±1.0 layers) remains constant. These clusters demonstrate efficient electrocatalytic activity in the hydrogen evolution reaction, probably at edge sites, confirming these new nanosystems as intriguing candidates for water splitting.

- [1] S. Pratontep, S. J. Carroll, C. Xirouchaki, M. Streun, and R. E. Palmer, Review of Scientific Instruments 76, 045103 (2005).
- [2] Z. W. Wang and R. E. Palmer, Nano Letters 12, 91 (2012).

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