

# Thursday Morning, November 1, 2012

## Surface Science

Room: 21 - Session SS+EN+OX-ThM

### Catalysis and Photocatalysis on Oxides

**Moderator:** Z. Dohnalek, Pacific Northwest National Laboratory

8:00am **SS+EN+OX-ThM1 Photoelectrochemical Water Splitting under Sunlight Irradiation using Oxynitride Electrodes Fabricated by Particle Transfer Method**, *K. Domen, J. Kubota*, The University of Tokyo, Japan  
**INVITED**

Hydrogen production through the photoelectrochemical (PEC) water splitting is one of the attractive ways to convert solar energy to storable chemical energy. The availability of powder semiconductor materials through coating methods for preparing photoelectrodes is a one of strong point of PEC cells. Even if the surface is a rough particle layer, the electrolyte solution automatically forms the desirable solid-liquid interface for whole semiconductor surfaces, where photoexcited carriers are separated by electric field.

Oxynitride and oxysulfide materials are promising candidates for photoelectrodes for water splitting. Among them,  $\text{LaTiO}_2\text{N}$  has a proper band structure from the view point of driving solar water splitting. The material shows photocatalytic hydrogen and oxygen evolutions in half reactions using sacrificial reagents, indicating that the material have a proper band structure to drive PEC water splitting.  $\text{LaTiO}_2\text{N}$  absorbs visible light up to 600 nm ( $E_g = 2.1$  eV), so that they can capture more solar energy than oxide photocatalysts, which typically have absorption in the UV region. Photoelectrodes based on the material have been studied extensively, however, the photocurrent was low due to the lack of good preparation method of the electrode.

In the present study, we report a novel fabrication method of photoelectrodes for PEC water splitting using semiconductor powders. This method, which we have termed the particle transfer (PT) method, is shown to be applicable to a variety of semiconductor powders.  $\text{LaTiO}_2\text{N}$  was demonstrated to exceed those prepared by the conventional method of photoelectrode fabrication from powder materials.

8:40am **SS+EN+OX-ThM3 Multi-step Photooxidation of CO on  $\text{TiO}_2(110)$** , *G.A. Kimmel, N.G. Petrik*, Pacific Northwest National Laboratory

$\text{TiO}_2$  is an important photocatalyst with many practical applications. However, a detailed understanding of the relevant physical and chemical processes for the photocatalysis remains elusive. We have studied the photooxidation of CO adsorbed on rutile  $\text{TiO}_2(110)$  during UV irradiation with  $\sim 1$  ms time resolution. Previous investigations with  $\sim 0.1$  s resolution found that the maximum  $\text{CO}_2$  photon-stimulated desorption (PSD) signal occurred for the first data point and then decreased monotonically with increasing irradiation time. However our experiments with improved time resolution show that the initial rate of  $\text{CO}_2$  production is zero, and then increases smoothly to a maximum before decreasing at longer irradiation times. Experiments varying the UV photon flux show that the  $\text{CO}_2$  PSD kinetics are proportional to the photon fluence but are independent of the photon flux (for the range investigated). The photon fluence required to reach the maximum  $\text{CO}_2$  PSD signal increases as the initial coverage of chemisorbed  $\text{O}_2$  increases – an effect that we attribute to changes in the initial charge state of the chemisorbed  $\text{O}_2$ . These results demonstrate that the production of  $\text{CO}_2$  proceeds through the formation of stable precursor. The angular distribution of the photodesorbing  $\text{CO}_2$ , which is peaked at  $\sim 40^\circ$  with respect to the surface normal perpendicular to the BBO rows, is also consistent with the production of  $\text{CO}_2$  from a precursor state. Previously, the photooxidation of CO on  $\text{TiO}_2(110)$  was believed to occur in a single non-thermal reaction step:  $\text{CO} + \text{O}_2 + h\nu \rightarrow \text{CO}_2 + \text{O}_{ad}$ . However, our results show that the photooxidation of CO requires at least two non-thermal reaction steps – one to form the precursor and a second to produce the  $\text{CO}_2$ . We will compare the experimental results to DFT calculations and discuss the role of photo-generated electrons and holes in the photooxidation of CO. These results show that the photooxidation of CO on  $\text{TiO}_2$  is more complicated than previously appreciated.

9:00am **SS+EN+OX-ThM4 Design of Band Engineered Photocatalysts using Titanium Dioxide**, *S.W. Ong, D.E. Barlaz, E.G. Seebauer*, University of Illinois at Urbana Champaign

Difficulties in achieving control over carrier concentration have impeded progress toward tailoring the electric fields in semiconducting oxide

photocatalysts based upon principles of electronic band engineering drawn from classical optoelectronics. The present work demonstrates such principles using the model case of methylene blue photo-oxidation over thin-film anatase  $\text{TiO}_2$  grown by atomic layer deposition. The carrier concentration in the polycrystalline semiconductor is controlled over a range of 2.5 orders of magnitude via an unconventional means - film thickness, which indirectly influences the concentration of electrically active donor defects at grain boundaries. Over this range, the reaction rate constant varies by more than a factor of 10, and is well described by a quantitative one-dimensional model for photocurrent. The model suggests that the changes in rate result fundamentally from variations in the width of the space charge layer near the surface. Electrical characterization of the films by capacitance-voltage measurements and ultraviolet photoelectron spectroscopy, together with detailed physical characterization by a variety of techniques, confirm this picture. Prospects for better control of grain boundary donor defects through film synthesis procedures are discussed.

9:20am **SS+EN+OX-ThM5 Adsorption of  $\text{CO}_2$  on Oxygen Precovered  $\text{TiO}_2(110)$  Surfaces**, *X. Lin, Y. Yoon, N.G. Petrik, G.A. Kimmel, Z. Li, Z.-T. Wang, B.D. Kay, I. Lyubimetsky, R. Rousseau, Z. Dohnalek*, Pacific Northwest National Laboratory

Rutile  $\text{TiO}_2(110)$  was employed as a model oxide surface to investigate the adsorption behavior of  $\text{CO}_2$  by means of scanning tunneling microscopy (STM) and density functional theory (DFT). STM images of partially reduced  $\text{TiO}_2(110)$  surfaces obtained before and after *in-situ* dosing of  $\text{CO}_2$  molecules at 50 K show that  $\text{CO}_2$  adsorbs preferentially on oxygen vacancy ( $\text{V}_\text{O}$ ) sites. Since the reaction of  $\text{CO}_2$  with oxygen adatoms (surface hydroxyl groups) may lead to the formation of carbonate (bicarbonate),  $\text{O}_2$  ( $\text{H}_2\text{O}$ ) was pre-dosed to form oxygen adatom (hydroxyl) covered  $\text{TiO}_2$  surfaces. On the oxygen precovered surfaces,  $\text{CO}_2$  molecules were found to preferentially bind on the Ti sites next to oxygen adatoms ( $\text{O}_\text{a}$ 's) and form  $\text{CO}_2/\text{O}_\text{a}$  complexes, while on hydroxylated surfaces no interactions were observed between  $\text{CO}_2$  and hydroxyl groups.  $\text{CO}_2$  binding to  $\text{O}_\text{a}$ 's is weak as revealed by the dissociation of the  $\text{CO}_2/\text{O}_\text{a}$  complexes at 50 K where  $\text{CO}_2$  diffuses away along the Ti row. The weak binding indicates that  $\text{CO}_2$  is bound to  $\text{O}_\text{a}$  only via dispersion forces. Temperature dependent studies (100 - 150 K) show that the  $\text{CO}_2$  binding energy next to  $\text{O}_\text{a}$ 's is smaller by  $\sim 20$  mV than that on  $\text{V}_\text{O}$ 's. At 50 K, however, the adsorption of  $\text{CO}_2$  on  $\text{V}_\text{O}$  is partially hindered by the higher adsorption barrier.  $\text{CO}_2$  molecules diffusing between two  $\text{CO}_2/\text{O}_\text{a}$  complexes are found to move fast compared to the STM sampling rate and are imaged as a time average of all  $\text{CO}_2$  binding configurations on Ti sites. DFT studies reveal the rotation-tumbling mechanism for  $\text{CO}_2$  diffusion with a very low diffusion barrier ( $\sim 50$  meV) in agreement with the experiment.

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9:40am **SS+EN+OX-ThM6 Probe of  $\text{NH}_3$  and CO Adsorption on the Very Outermost Surface of a Porous  $\text{TiO}_2$  Adsorbent Using Photoluminescence Spectroscopy**, *A. Stevanovic, J.T. Yates, Jr.*, University of Virginia

The photoluminescence (PL) of powdered  $\text{TiO}_2$  at 529.5 nm (2.34 eV) has been found to be a sensitive indicator of UV-induced band structure modification. As UV irradiation occurs, the positive surface potential changes and shifts the depth of the depletion layer. It was found that UV light (3.88 eV) induces a positive surface potential which diminishes band bending in n-type  $\text{TiO}_2$  and enhances PL1. Also, adsorbates modify the PL intensity by exchanging charge with  $\text{TiO}_2$ , producing a change in the surface band bending structure.

In addition, we employ photoluminescence (PL) spectroscopy to probe the development of adsorbed layers on the very outermost surface sites of a porous solid adsorbent ( $\text{TiO}_2$ ) in a depth of 20 nm where the meso-pores, separating 30-80 nm  $\text{TiO}_2$  particles, join the gas phase. In parallel, we also employ transmission infrared (IR) spectroscopy to gain insight into the extent of adsorption averaged over the entire depth of the diffusion process. The combination of the two surface spectroscopies (PL and IR) allows one to observe the kinetics of transport of adsorbate molecules between the very outermost surface region (where adsorption

first occurs) and the interior of the powdered substrate. The transport is governed by the surface mobility of the adsorbate molecules, and hysteresis effects in adsorption/desorption are observed.

References:

1. Stevanovic, A.; Buttner, M.; Zhang, Z.; Yates, J. T., Jr., Photoluminescence of TiO<sub>2</sub>: effect of UV light and adsorbed molecules on surface band structure. *Journal of the American Chemical Society* **2012**, *134*, (1), 324-32.
2. Stevanovic, A.; Yates, J. T., Jr., Probe of NH<sub>3</sub> and CO Adsorption on the Very Outermost Surface of a Porous TiO<sub>2</sub> Adsorbent Using Photoluminescence Spectroscopy. *Langmuir: the ACS journal of surfaces and colloids* **2012**, *28*, (13), 5652-9.

Work supported by the Army Research Office.

10:40am **SS+EN+OX-ThM9 Site-Specific Photocatalytical Reactions of O<sub>2</sub> on TiO<sub>2</sub>(110)**, **Z.-T. Wang**, Pacific Northwest National Laboratory, N.A. Deskins, Worcester Polytechnic Institute, I. Lyubinskyy, Pacific Northwest National Laboratory

Photo-stimulated reactions on TiO<sub>2</sub> have attracted much attention due to the variety of potential applications ranging from a hydrogen production by water splitting to environmental remediation through organic pollutant oxidation. In majority of these processes, the oxygen plays a crucial role. A better understanding of the fundamental aspects of oxygen on TiO<sub>2</sub> can potentially lead to improvements or developments of the TiO<sub>2</sub> applications. We present the direct observation at an atomic level with high-resolution scanning tunneling microscopy of photostimulated reactions of single O<sub>2</sub> molecules on reduced TiO<sub>2</sub>(110) surfaces at 50 K. The critical relation between photoreactivity and adsorption sites on TiO<sub>2</sub> is demonstrated. Two distinct reactions of O<sub>2</sub> desorption and dissociation occur at different active sites of terminal Ti atoms and bridging O vacancies, respectively. These two reaction channels follow very different kinetics. While hole-mediated O<sub>2</sub> desorption is promptly and fully completed, electron-mediated O<sub>2</sub> dissociation is much slower and is quenched above some critical O<sub>2</sub> coverage. Density functional theory calculations indicate that both coordination and charge state of an O<sub>2</sub> molecule chemisorbed at specific site largely determine a particular reaction pathway.

11:00am **SS+EN+OX-ThM10 Bond Selectivity in the Activation of n-alkanes on PdO(101)**, **J.F. Weaver**, A. Antony, C. Hakanoglu, F. Zhang, University of Florida, A. Asthagiri, The Ohio State University

We have investigated initial C-H bond selectivity in the activation of propane and n-butane on PdO(101) both experimentally and computationally. Temperature-programmed experiments using different propane isotopologues reveal a strong preference toward primary C-H bond cleavage of propane on PdO(101); about 90% of the propane molecules which react do so by primary C-H bond activation. Direct measurements of the initial dissociation probability of various n-butane isotopologues also demonstrate a high selectivity for primary C-H bond activation of n-butane on PdO(101) at low coverages. Unlike propane, however, TPRS experiments show that the preference for primary C-H bond cleavage of n-butane diminishes with increasing molecular coverage. Calculations using dispersion-corrected DFT reproduce the selectivity toward primary C-H bond cleavage of propane and n-butane on PdO(101), and predict that alkane C-H bond scission occurs heterolytically on the oxide surface. The calculations suggest that greater substituent polarization in the 1-alkyl transition structures is responsible for the lower energy barriers for primary vs. secondary C-H bond activation of alkanes on PdO(101).

11:20am **SS+EN+OX-ThM11 Photoresponse, Electronic Transport and Magnetic Properties of Ti-doped (Cr<sub>x</sub>Fe<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub>**, **S.E. Chamberlin**, T.C. Kaspar, M.E. Bowden, V. Shutthanandan, S.A. Chambers, M.A. Henderson, Pacific Northwest National Laboratory

There is widespread interest in discovering materials that can effectively harvest sunlight in the visible region of the electromagnetic spectrum in order to drive chemical processes on surfaces. Hematite (Fe<sub>2</sub>O<sub>3</sub>) has received renewed interest recently as the active photoanode in photoelectrochemical (PEC) water splitting to store solar energy as H<sub>2</sub>. Hematite has three key advantages which make it appealing: it is very abundant, it has a bandgap of 2.2 eV, which is suitably narrow to harvest incident solar radiation, and it is sufficiently stable in the aqueous solutions required for PEC water splitting. However, hematite is a charge-transfer insulator with extremely poor electron and hole mobilities, which results in short hole diffusion lengths and ultrafast recombination of photogenerated electron/hole pairs before charge separation can occur. Substitutional Ti(IV) at an Fe(III) site should be a donor, and epitaxial Ti-doped α-Fe<sub>2</sub>O<sub>3</sub> exhibits significantly enhanced conductivity relative to pure hematite when grown under certain conditions by oxygen-assisted molecular beam epitaxy (OAMBE) on α-Al<sub>2</sub>O<sub>3</sub>(0001) substrates.<sup>1</sup> In addition, Mashiko *et al.*<sup>2</sup> have

shown that the bandgap of pure hematite can be reduced to 1.7 eV by alloying with Cr(III) in epitaxial films. Combining these approaches is expected to result in material with both a reduced bandgap and favorable electrical conductivity, which will facilitate visible-light photoactivity. Heteroepitaxial thin films of (Fe<sub>1-x</sub>Cr<sub>x</sub>)<sub>2</sub>O<sub>3</sub> and (Fe<sub>1-x</sub>Cr<sub>x</sub>Ti<sub>y</sub>)<sub>2</sub>O<sub>3</sub> were deposited on α-Al<sub>2</sub>O<sub>3</sub>(0001) substrates by OAMBE. Film quality was monitored *in situ* by reflection high energy electron diffraction (RHEED). *In situ* x-ray photoemission spectroscopy (XPS) was utilized to characterize the charge states of the cations. Film crystallinity and lattice parameters were determined *ex situ* by high resolution x-ray diffraction (HRXRD). Rutherford backscattering spectrometry (RBS) in both random and channeling geometries confirmed the film stoichiometry, and elucidated the degree of substitution of the cations in the lattice. Preliminary optical absorption measurements and photochemistry experiments will be presented.

1. B. Zhao, T. C. Kaspar, T. C. Droubay, J. McCloy, M. E. Bowden, V. Shutthanandan, S. M. Heald, and S. A. Chambers, *Phys. Rev. B* **84**, 245325 (2011).

2. H. Mashiko, T. Oshima, and A. Ohtomo, *Appl. Phys. Lett.* **99**, 241904 (2011).

11:40am **SS+EN+OX-ThM12 A Nonadiabatic Mechanisms of Inequilibrium Charge Carriers Production in Pd/n-GaP Schottky Nanodiode Exposed to Atomic Hydrogen**, **S.V. Simchenko**, V. Styrov, Azov State Technical University, Ukraine

Since the recent discovery of production of electronic flows in Schottky diodes with nanosized “top” metal layer due to ballistic metal-to-semiconductor transport of hot electrons formed by the surface exoergic chemical reaction, e.g. [1], this effect attracts attention of scientists owing to its fundamental and practical potential. Here we investigate a new system of that kind, namely Pd-(n)GaP planar Schottky diode (15 nm Pd-layer) placed in the atmosphere of atomic hydrogen. We found the steady-state current flow through the system under consideration in perpendicular direction to the metal surface on which the hydrogen atoms stationary recombine into molecules.

We elaborated a new approach to detect production of the inequilibrium charge carriers via nonadiabatic channel by observing the current-voltage characteristic of the Schottky diode in the presence and absence of the atomic flux incident on the structure. The nonequilibrium nature of the additional carriers is confirmed by kinetics measurements: the current drops to its initial value in the absence of atoms practically momentarily once the atoms are “switched off” and jumps immediately to its excited value when atoms are “switched on” (at the given temperature of the structure and the fixed forward voltage bias on the structures). We were able to draw some quantitative information about the processes of generation of nonequilibrium electron-hole pairs in the reaction of recombination of hydrogen atoms on Pd-surface and their transport in the metal film. The short circuit current is expressed in terms of yield of the chemoexcited carriers and probability of their survival while traveling through the Pd-film.

For a 1V forward bias the current drastically grows from 3 nA to 950 μA; thus the bias allows gaining chemi-current value as large as five orders of magnitude. This result can be of significant importance for the practical applications of the nonequilibrium chemi-conductance and chemi-currents in Schottky nanostructures including sensing and chemical-to-electricity energy conversion.

[1] B. Georgen, H.Nienhaus, W.H. Weinberg, E. McFarland. *Science*, **294**, 2521 (2003)

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