Surface Science Division
Room D136 - Session SS+HC-TuA

Photochemistry

Moderators: Erik Jensen, University of Northern British Columbia, **Ahmad Nawaz**, Hebrew University of Jeruzalem

2:20pm **SS+HC-TuA-1 Pt Nanoclusters on GaN Nanowires for Solar-Assisted Seawater Hydrogen Evolution***, **Victor Batista**, W. Dong, Y. Xiao, K. Yang, Z. Ye, P. Zhou, I. Navid, Z. Mi,* Yale University **INVITED**

Seawater electrolysis provides a viable method to produce clean hydrogen fuel. To date, however, the realization of high-performance photocathodes for seawater hydrogen evolution reaction has remained challenging. Here, we introduce n+-p Si photocathodes with dramatically improved activity and stability for hydrogen evolution reaction in seawater, modified by Pt nanoclusters anchored on GaN nanowires (Fig 1). We find that Pt-Ga sites at the Pt/ GaN interface promote the dissociation of water molecules and spilling H* over to neighboring Pt atoms for efficient H2 production. Pt/GaN/Si photocathodes achieve a current density of −10 mA/cm2 at 0.15 and 0.39 V vs. RHE and high applied bias photon-to-current efficiency of 1.7% and 7.9% in seawater (pH = 8.2) and phosphate-buffered seawater (pH = 7.4), respectively. We further demonstrate a record-high photocurrent density of ~169 mA/cm2 under concentrated solar light (9 suns). Moreover, Pt/GaN/Si can continuously produce H2 even under dark conditions by simply switching the electrical contact. This work provides valuable guidelines to design an efficient, stable, and energy- saving electrode for H2 generation by seawater splitting.

3:00pm **SS+HC-TuA-3 Photoreactivity of Single Micro-Sized TiO_2 Crystals***, H. Zhu, W. Lu, K. Park, **Zhenrong Zhang**,* Baylor University

Understanding the reactivity of TiO_2 particles with different polymorphs and morphologies is important for many photocatalytic applications. Here, the reactivity of individual anatase TiO_2 microcrystals with a large percentage of (001) facet was monitored and studied using operando photoluminescence microscopy. The photoreduction of resazurin on anatase microcrystals shows that the photoreduction rate on each microcrystal was different although the microcrystals had comparable sizes and exposed the same facets. The reaction rate changes from no reactivity to higher than that of the anatase (001) bulk single crystal. The reaction rate of the anatase microcrystals depends on the morphology and the structure of each particle. The reactivities of the microcrystals with mixed anatase-rutile phases and after the anatase-to-rutile phase transformation have also been monitored.

3:20pm **SS+HC-TuA-4 Electron Induced Photochemistry of Nitrous Oxide-Water Co-Adsorbed Film (N_2O@H_2O) as a Model Study of Astrochemistry in the Interstellar Medium***, **Ahmad Nawaz**,* The Hebrew University of Jerusalem, Israel

The desorption kinetics of N_2O@H_2O film deposited on a Ru (0001) surface under ultra-high vacuum (UHV) environment (2×10^{-10} Torr) has been investigated as a model study for electrons-induced reactivity that takes place in the interstellar medium, using temperature-programmed desorption (TPD) measurements, at substrate temperature of 35K. The TPD spectra of all the prominent product masses were well detected by the QMS, employing a 3D-TPD analysis. The N_2O molecules, embedded within ASW as the host matrix, decompose upon exposure to electrons at kinetic energies of 10eV and 50 eV. This leads to the formation of new molecular products at m/z values of 28 (N_2) and 30 (NO) as the primary products. Typical TPD spectra of the parent N_2O molecules, while embedded in ASW layer (15 ML) are shown in Figure 1a and product formation is shown in Figure 1b. Here, the primary N_2O TPD peaks appear at ~82K, while some of these molecules are trapped within the water film and desorb together with the main ASW film at ~160K.

4:20pm **SS+HC-TuA-7 Structure and Chemistry of Aqueous Oxide Interfaces from Molecular Simulations***, A. Selloni, A. Raman,* Princeton University*; **Marcos Calegari Andrade**,* Lawrence Livermore National Laboratory*; B. Wen,* Henan University, China **INVITED**

Photo-electrocatalysis involving complex oxide-water interfaces is a highly promising technology for the sustainable production of fuels. However, probing these complex interfaces and gaining atomistic insights is still very challenging for current experimental methods, and is often only possible through accurate computational simulations. In this talk I will discuss some of our recent work on the application of ab-initio based molecular simulations to understand the structure and dynamics of interfacial water on photoelectrochemically relevant oxide surfaces. Specific topics will include proton transfer at the aqueous TiO_2 and IrO_2 interfaces and the influence of surface atomic structure on the water dissociation fraction and hydroxyl lifetimes at the interface.

5:00pm **SS+HC-TuA-9 Photodissociation of an Adsorbate via Coadsorbate Photon Absorption: Electronic Energy Transfer in Heterogeneous Molecular Thin Films***, **Erik Jensen**,* University of Northern B.C., Canada

The photophysics of many small aromatics and related molecular systems has been studied intensely and widely for many years, both in understanding the molecular origins of natural phenomenon such as photosynthesis, as well as in areas of technological interest. Although the UV photosensitization of CH_3I dissociation in gas-phase mixtures with benzene was noted many years ago[1], we can find no subsequent examples of studies of the photochemical dynamics of this process. We have studied a set of thin film molecular systems on a metal substrate using UHV surface science techniques and time-of-flight spectroscopy on neutral photofragments.

In the present work, we have studied the dynamics of the near-UV photodissociation of CH_3I adsorbed on thin films (1–10ML) of benzene[2] and a variety of fluorinated benzenes grown on a Cu(100) substrate. Using polarized 248nm light, we find that the kinetic energies of the CH_3 photofragments point to significantly altered CH_3I dissociation dynamics when adsorbed on C_6H_6, C_6H_5F and $C_6H_4F_2$ thin films, with progressive changes in the observed dynamics as higher fluorobenzenes are used (up to C_6F_6). The altered CH_3I photodissociation dynamics and coincidently increased effective photodissociation cross sections are ascribed to a new pathway with initial photoabsorption in the aromatic thin film, and the excitation energy being efficiently transported to the CH_3I adsorbed on top. There is evidence that excitons in the aromatic thin film play a significant role in the transport and transfer of the electronic excitation to the CH_3I top layer.

References

[1] Dubois, J.T. and Noyes Jr., W.A., *Photochemical Studies XLVI: Photosensitization by Benzene and Pyridine Vapours*, J. Chem. Phys. **19**, 1512 (1951).

[2] Jensen, E.T., *Contrasting Mechanisms for Photodissociation of Methyl Halides Adsorbed on Thin Films of C_6H_6 and C_6F_6*. Phys. Chem. Chem. Phys. **23**, 3748 (2021).

5:20pm **SS+HC-TuA-10 UV-Induced Oxidation of Aluminum***, **Robert Berg**, C. Tarrio, T. Lucatorto,* National Institute of Standards and Technology (NIST)*; F. Eparvier, A. Jones,* Laboratory for Atmospheric and Space Physics

Aluminum oxide films are usually grown on aluminum metal by anodization in a liquid electrolyte (thick films) or heating in the presence of oxygen gas (thin films). A third way is to expose the aluminum to ultraviolet radiation (UV) in the presence of water vapor. We devised a model of such oxidation that combined descriptions of photoemission from the Al metal, electron-phonon scattering in the oxide, Al^{3+} ion transport in the oxide, and the adsorption and ionization of H_2O on the oxide surface. It also accounted for UV-induced desorption of H_2O and the effect of the Al^{3+} ion flux on the surface reactions.

The model's five free parameters were fit to our measurements of UV-induced oxidation of aluminum. The UV, which was produced by filtering synchrotron radiation, comprised wavelengths from 150 nm to 480 nm, and the H_2O pressure was varied between 3×10^{-8} mbar and 1×10^{-4} mbar. Exposures lasted from 3 hours to 20 days. An exposure with oxygen instead of water caused oxidation consistent with the background H_2O pressure; the oxygen caused no additional oxidation.

The parameter values fitted to our measurements allowed us to describe the oxidation of aluminum membranes that were used to filter extreme UV wavelengths on the Solar Dynamics Observatory, a sun-observing satellite. This new understanding will help prevent similar problems on future satellites. These results are the first experimental confirmation of a model of UV-induced oxidation.

5:40pm **SS+HC-TuA-11 Self-Induced and Progressive Photo-Oxidation of Organophosphonic Acid Grafted Titanium Dioxide*, Nick Gys,*** Vrije Universiteit Brussel, Belgium*; B. Pawlak,* Hasselt University, Belgium*; K. Marcoen,* Vrije Universiteit Brussel, Belgium*; G. Reekmans,* Hasselt University, Belgium*; L. Fernandez Velasco,* Royal Military Academy, Belgium*; R. An,* University of Antwerp, Belgium*; K. Wyns,* Flemish Institute for Technological Research, Belgium*; K. Baert,* Vrije Universiteit Brussel, Belgium*; K. Zhang, L. Lufungula,* University of Antwerp, Belgium*; A. Piras,* Hasselt University, Namur University, Belgium*; L. Siemons,* University of Antwerp, Belgium*; B. Michielsen,* Flemish Institute for Technological Research, Belgium*; S. Van Doorslaer, F. Blockhuys,* University of Antwerp, Belgium*; T. Hauffman,* Vrije Universiteit Brussel, Belgium*; P. Adriaensens,* Hasselt University, Belgium*; S. Mullens,* Flemish Institute for Technological Research, Belgium*; V. Meynen,* University of Antwerp, Belgium

The introduction of organic molecules onto the surface of metal oxides through surface grafting provides the ability to tailor the surface properties towards an increased specificity and control of interactions. In the field of hybrid organic-inorganic materials, organophosphonic acid (PA) grafted metal oxides are becoming increasingly more prominent given their versatility in surface tuning and their specific merits in applications ranging from supported metal catalysis(*1*), hybrid (photo)-electric devices(*2*), biosensing(*3*) and sorption and separation processes.(*4*) While synthesis-properties-performance correlations are being studied for organophosphonic acid grafted TiO_2, their stability and the impact of exposure conditions on possible changes in the interfacial surface chemistry remain unexplored. In addition, a differentiation in the stability of the organic group (carbon chain) and the M-O-P bonds is missing. In this study(*5*), the impact of different ageing conditions on the evolution of the surface properties of propyl- and 3-aminopropylphosphonic acid grafted mesoporous TiO_2 over a period of 2 years is reported, using solid-state ^{31}P and ^{13}C NMR, ToF-SIMS, EPR and XPS as main techniques. In humid conditions under ambient light exposure, PA grafted TiO_2 surfaces initiate and facilitate photo-induced oxidative reactions, resulting in the formation of phosphate species and degradation of the grafted organic group with a loss of carbon content ranging from 40 to 60 wt%. Since exposure under dry air does not result in ageing phenomena, humidity and more specifically, the interactions of adsorbed water with the grafted surface, play a fundamental role in the ageing process. By revealing the underlying ageing mechanism, solutions were provided to prevent degradation. This work creates critical awareness in the research community working on hybrid titania materials and other possible photo-active materials to evaluate changes in photo-activity and stability after surface grafting.

1. F. Forato et al., Chem. - A Eur. J. 24, 2457–2465 (2018).

2. H. Chen, W. Zhang, M. Li, G. He, X. Guo, Chem. Rev. 120, 2879–2949 (2020).

3. N. Riboni et al., RSC Adv. 11, 11256–11265 (2021).

4. G. A. Seisenbaeva et al., RSC Adv. 5, 24575–24585 (2015).

5. N. Gys et al., Chempluschem. 88 (2023), doi:10.1002/cplu.202200441.

6:00pm **SS+HC-TuA-12 "Laser-XPS" invented 1989 in Japan, Patented 1997*, B. Vincent Crist,*** XPS Library

In 1989, a novel technique, Laser-XPS, was developed. Laser-XPS uses XPS to probe the core level surface chemical physics of various solid state materials while the materials are held in an ultra-high vacuum (UHV) chamber and irradiated with CW tunable organic dye or argon ion lasers. These two tunable CW lasers provide energy in the 1.9-3.5 eV range (655-351 nm, 44-81 Kcal/mol) with power levels ranging from 100-1,000 mW. A dynamicmode of operation uses XPS to directly measure the electronic nature of the photo-excited states, the photo-thermal effects, and the lifetimes of the associated initial and final states produced by the tunable CW laser irradiation. Several reversible phenomena, which are wavelength or power level dependent, were observed via the dynamic mode. These phenomena include: energy shifts in XPS signals, changes in XPS peak widths, charge control quality, and phosphorescence during XPS.A sequential mode of operation makes it possible to study the non-reversible effects of irradiating materials under UHV conditions with CW lasers. Non-reversible phenomena observed via the sequential mode include: surface chemical reactions, elimination of adventitious carbon contamination, elimination of oxygen species associated with the presence of water, hydroxides, or carbonates, color changes, outgassing, and melting. The initially expected energy shifting of a specific XPS signal within a complex spectrum of XPS signals from very similar chemical species due to narrow,selectivephoto-excitation of specific valence bands, was, however, not realized in this preliminary study.

Author Index

Bold page numbers indicate presenter