

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room A213 - Session HC+SS-FrM

Catalysis at Complex Interfaces

Moderators: Elizabeth Landis, College of the Holy Cross, Fan Yang, Dalian Institute of Chemical Physics, China

8:20am **HC+SS-FrM-1 Pd Nanoparticles on Alumina Nanofibers by Electrospinning for Heterogeneous Catalysis, Miguel Angel Rodriguez Olguin, M Enes da Silva, J Faria, A Susarrey Arce, H Gardeniers, University of Twente, Netherlands**

The pressing transition from unsustainable fossil fuels to a sustainable economy based on renewables with minimal chemical waste is one of the grand challenges for the twenty-first century. To mitigate these challenges, it is crucial that improved synthetic catalytic methods are developed, that increase conversion and selectivity of existing chemical transformation processes. For example, *alumina* is a widely used catalyst support owing to its excellent thermal stability and inherent chemical acidity. Technologies like three-way catalytic converters rely on well-defined alumina-based structured monoliths of about hundred of micrometers to millimeters dimensions without spatial control on the allocation of the metal catalyst. The latter is considered essential to derive at more stable catalysts, it may prevent sintering for instance. Additive manufacturing of catalyst materials can pave the path to control the distribution of catalytic nanoparticles, and mass transport modulation by optimized 3-dimensional support designs. In this work, we present co-axial electrospinning to control the distribution of Pd nanoparticles (Pd NPs) over synthetic fibrous-like Al_2O_3 structures. First, our approach involved several synthetic routes for the fine tuning of the Al_2O_3 fibers by varying the formulation of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Al}(\text{OH})_3$, $\text{C}_{14}\text{H}_{27}\text{AlO}_5$ precursors and Al_2O_3 nanoparticles additives. Thermal stability and chemical properties of the nanofibers have been tested. The Al_2O_3 fibers morphology is visualized with Scanning Electron Microscopy (SEM), and the fiber diameter is estimated between 81 nm to 107 nm depending on aluminum precursor. Furthermore, X-ray Diffraction (XRD) is utilized to confirm the crystalline phase of the Al_2O_3 used as support. Second, the Al_2O_3 that performs best in terms of morphology, crystallinity, surface area and acidity is loaded with Pd NPs. The location of Pd NPs is varied by tuning the Pd concentration of the precursor suspension. Finally, the Al_2O_3 -Pd fibrous catalyst is tested by chemisorbing CO species. CO chemisorption in liquid phase is performed with *in-situ* Attenuated Total Reflectance Infrared Spectroscopy (ATR-IR). Further, liquid phase catalytic reactions will be explored.

8:40am **HC+SS-FrM-2 Multi-Layered TiO_2 Nanofibrous Structures Decorated with Catalytic Nanoparticles for Photoelectrocatalytic Applications, Cristian Deenen, C Eyövge, A Susarrey-Arce, H Gardeniers, University of Twente, Netherlands**

Electrospinning is a technique to fabricate nanofibers by applying a high potential between a nozzle and a collector. As a solution is pumped through the nozzle, a jet is ejected from the nozzle that solidifies as it moves towards the collector, resulting in nanofiber deposition on the collector.

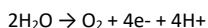
A drawback in conventional electrospinning setups consisting of a singular electrified nozzle is the difficulty in depositing multiple material combinations due to the time and labor required to either manually replace the nozzle or to flush the fluidic elements of the electrospinning setup. A novel multi-nozzle approach will be demonstrated to reduce the time required for the switching of precursor materials from minutes to seconds. The proposed concept opens up new possibilities for the fabrication of complex devices with a variety of material formulations, such as alternating functional layers of interest to the fields of catalysis, electrochemistry and photovoltaics.

Mounting multiple nozzles on a rotating disc allows the inactive nozzles to be rotated out-of-plane, away from the electric field between the active nozzle and the collector, which at the same time reduces the risks of dripping from the inactive nozzles. Combining this concept with appropriate control of electrical voltages and fluidic flow through the different nozzles, allows the engineering of a flexible platform for fast and reliable manufacturing of multi-component materials using electrospinning. In this work, we will demonstrate the instrumental concept and apply it to the fabrication of catalytic layers composed of TiO_2 , decorated with three different metal catalyst nanoparticles (Au, Pd, Pt)

which function in concert for light harvesting and efficient hydrogen production during photoelectrocatalysis.

9:00am **HC+SS-FrM-3 Water Oxidation Reaction in Natural Photosynthesis, Junko Yano, Lawrence Berkeley National Laboratory INVITED**

Many of the catalytic reactions in inorganic systems and natural enzymes involve multiple electrons, and proceed through several intermediate steps. For example, photosynthetic water oxidation in nature is catalyzed by the metal center that consists of oxo-bridged four Mn and one Ca atoms, which is located in multi-subunit membrane protein, Photosystem II (PSII). This is one of the most important, life-sustaining chemical processes occurring in the biosphere. The oxygen-evolving complex (OEC) in PSII, which contains the heteronuclear Mn_4CaO_5 cluster, catalyses the reaction



that couples the four-electron oxidation of water with the one-electron photochemistry occurring at the PSII reaction center. The OEC cycles through five intermediate S-states (S_0 to S_4) that corresponds to the abstraction of four successive electrons from the OEC (Fig. 1). Once four oxidizing equivalents are accumulated (S_4 -state), a spontaneous reaction occurs that results in the release of O_2 and the formation of the S_0 -state.

Recently, the development of X-ray Free Electron Lasers (XFELs) has opened up opportunities for studying the dynamics of biological systems. Intense XFEL pulses enable us to apply both X-ray diffraction and X-ray spectroscopic techniques to dilute systems or small protein crystals. By taking advantage of ultra-bright femtosecond X-ray pulses, one can also collect the data under functional conditions of temperature and pressure, in a time-resolved manner, after initiating reactions, and follow the chemical dynamics during catalytic reactions and electron transfer. Such an approach is particularly beneficial for biological materials and aqueous solution samples that are susceptible to X-ray radiation damage.

We have developed spectroscopy and diffraction techniques necessary to fully utilize the capability of the XFEL x-rays for a wide-variety of metalloenzymes, like Photosystem II, and to study their chemistry under functional conditions. One of such methods is simultaneous data collection for x-ray crystallography and x-ray spectroscopy, to look at overall structural changes of proteins and chemical changes at metal catalytic sites. We have used the above techniques to study the water oxidation reaction of Photosystem II, in which the Mn_4CaO_5 cluster catalyzes the reaction. The current status of this research and the mechanistic understanding of the water oxidation reaction based on the X-ray techniques is presented.

9:40am **HC+SS-FrM-5 Synthesis and Characterization of Carbon-supported PdCu Nanoparticles for the Water Electrolysis in Acid Medium, Jonder Morais, D Lima, M Castegnaro, M Alves, Universidade Federal do Rio Grande do Sul, Brazil**

Hydrogen is an important option for an energetic vector due to its high energy density, high heat of combustion and it can be produced in different ways, such as water electrolysis, which is a clean and efficient process. It generates pure H_2 and the required energy for the process can be obtained from renewable sources. However, it is essential to find efficient catalytic materials to be applied as the electrodes for the water electrolysis that usually involves the use of noble metals. An important alternative to lower the production costs for the electrode material is the development of bimetallic nanoparticles supported on amorphous conducting carbon. Recently, a catalyst composed by carbon-supported bimetallic PdCu alloy nanoparticles presented significant activity in the oxygen oxidation reaction [1]. In this sense, PdCu based electrocatalysts were synthesized accordingly and the morphology, composition and structure of PdCu nanoparticles were characterized by TEM, EDS and XRD, respectively. Cathodes were prepared by the brushing technique with the electrocatalyst [2] and tested in the hydrogen evolution reaction (HER) employing 0.5 M H_2SO_4 aqueous solution as the electrolyte. Cyclic voltammetry, chronoamperometry and Tafel analysis were carried out to evaluate the stability, reaction mechanism determination and efficiency of HER. Moreover, XPS measurements were performed on the PdCu cathodes before and after the electrochemical measurements in order to monitor the modifications on the electronic structure of the electrocatalyst. Cyclic voltammetry analysis of the cathode showed that the system rapidly becomes highly stable. Tafel analysis indicated that for this system, the mechanism of the reaction is that of Volmer-Heyrovsky, where the H^+ desorption is the determining step. The reaction exchange current density of HER for PdCu was around 0.8 mA cm^{-2} , in the equilibrium potential of -270 mV_{SCE}. Moreover, the current density observed in the chronoamperometry analyzes at -2 V_{SCE} was around

Friday Morning, October 25, 2019

340 mA cm⁻². XPS analysis showed a significant change in the copper structure after the hydrogen evolution reaction, indicating that it assumed a more metallic character after the reaction. The obtained results indicate that the PdCu carbon-supported bimetallic nanoparticles are a very promising electrocatalysts and should be further studied.

Financial support from CAPES and CNPq is acknowledged.

[1] M. V. Castegnaro, J. Morais et al, *Langmuir* 33 (2017) 2734-2743

[2] D. W. Lima, E. M. A. Martini et al, *J. Int. J. Hydrogen Energy* 42 (2017) 5676-5683

10:00am **HC+SS-FrM-6 Nanoscale Spectromicroscopy and Chemical Activity of Bilayer Silicate Films on Pd(100) and Pd(111)**, *Samuel Tenney, C Eads*, Brookhaven National Laboratory; *L Mark*, University of Colorado at Boulder; *V Lee*, University of North Texas; *M Wang*, Brookhaven National Laboratory; *J Medlin*, University of Colorado at Boulder; *J Kelber*, University of North Texas; *D Stacchiola*, Brookhaven National Laboratory

In this talk we present the first reported photothermal infrared (PTIR) spectra and hyperspectral images of ultrathin bilayer silicate films with a spatial resolution better than 10nm and compare this with traditional infrared reflection absorption spectroscopy (IRRAS) of the same surface. The growth of the ultrathin bilayer silicates on Pd(100) and Pd(111) surfaces was observed in real-time with an in-situ low energy electron microscope (LEEM) capable of selected area low energy electron diffraction (μ -LEED). The samples were further probed with ambient pressure X-ray photoelectron spectroscopy (AP-XPS), temperature programmed desorption (TPD) and high resolution electron energy loss spectroscopy (HREELS). The chemical activity and enhanced selectivity of these model silicate/Pd catalysts will be discussed.

10:20am **HC+SS-FrM-7 Formation and Properties of Mirror Twin Grain Boundary Networks in Molybdenum Dichalcogenides**, *Matthias Batzill*, University of South Florida

INVITED

Edges, defects, and dopants in 2D transition metal dichalcogenides have been shown to give rise to special chemical, electronic, and magnetic properties in these materials. To utilize the potential of these modifications a detailed understanding of their controlled formation and atomic scale properties is needed. In this talk we present our studies on the controlled formation of metallic mirror twin grain boundaries (MTBs) in MoSe₂ [1] or MoTe₂ [2] by incorporation of excess Mo into the lattice. Very high density of MTB networks can be obtained in MoTe₂ that effectively metallizes the material and thus may act as a metallic contact patch [3]. Such line defects may also increase electrocatalytic properties for hydrogen evolution reactions [4]. On a more fundamental level, we show that these 1D metallic grain boundaries host one dimensional electron gas and we present the first angle resolved photoemission (ARPES) studies of such line defects. These studies show evidence for the presence of Tomonaga-Luttinger Liquid behavior of 1D electron systems [5]. Finally, we show that other transition metals may also be incorporated into MoTe₂ and the incorporation of vanadium induces room temperature ferromagnetic ordering and thus is an example of a 2D dilute ferromagnetic semiconductor [6].

[1] Y Ma, S Kolekar, H Coy Diaz, J Aprozanz, I Miccoli, C Tegenkamp, M Batzill. Metallic Twin Grain Boundaries Embedded in MoSe₂ Monolayers Grown by Molecular Beam Epitaxy. *ACS Nano* 11, 5130-5139 (2017)

[2] HC Diaz, Y Ma, R Chaghi, M Batzill. High density of (pseudo) periodic twin-grain boundaries in molecular beam epitaxy-grown van der Waals heterostructure: MoTe₂/MoS₂. *Appl. Phys. Lett.* 108, 191606 (2016)

[3] PM Coelho, HP Komsa, H Coy Diaz, Y Ma, AV Krasheninnikov, M Batzill. Post-Synthesis Modifications of Two-Dimensional MoSe₂ or MoTe₂ by Incorporation of Excess Metal Atoms into the Crystal Structure. *ACS Nano* 12, 3975-3984 (2018).

[4] T Kosmala, H Coy Diaz, HP Komsa, Y Ma, AV Krasheninnikov, M Batzill, S Agnoli. Metallic Twin Boundaries Boost the Hydrogen Evolution Reaction on the Basal Plane of Molybdenum Selenotellurides. *Adv. Energy Mat.*, 1800031 (2018).

[5] Y Ma, et al. Angle resolved photoemission spectroscopy reveals spin charge separation in metallic MoSe₂ grain boundary. *Nature Commun.* 8, 14231 (2017).

[6] PM Coelho, et al. Room temperature ferromagnetism in MoTe₂ by post-growth incorporation of vanadium impurities. *Adv. Electr. Mat.* in press.

11:00am **HC+SS-FrM-9 Selectable Catalytic Reduction of Carbon Dioxide to Formic Acid or Methanol over Defect Hexagonal Boron Nitride***, *K Chagoya, T Jiang, D Nash, D Le, Talat S. Rahman, R Blair*, University of Central Florida

Finding effective heterogeneous catalysts, consisting of abundant elements, for the hydrogenation of waste gas carbon dioxide into value added molecules is a challenging task for global energy and sustainability solutions. In a closely coupled computational and experimental effort, we find that vacancies induced in defect-laden hexagonal boron nitride (*dh*-BN) can effectively activate the CO₂ molecule for hydrogenation. Computationally, we demonstrate that activation occurs through back-donation to the π^* orbitals of CO₂ from frontier orbitals (defect state) of the *h*-BN sheet localized near a nitrogen vacancy (V_N). Subsequent hydrogenation to formic acid (HCOOH) and methanol (CH₃OH) occurs through vacancy facilitated co-adsorption of hydrogen and CO₂. More importantly, we find that *dh*-BN is a temperature-driven switchable catalyst with formic acid formation observable at reaction temperatures above 160 °C and pressures of 583 kPa, while methanol formation was observed at lower temperatures (as low as 20 °C), which are in great agreement with thermodynamics and kinetics of our calculated reaction pathways.

*Work supported in part by DOE grant DE-FG02-07ER15842

Author Index

Bold page numbers indicate presenter

— A —

Alves, M: HC+SS-FrM-5, **1**

— B —

Batzill, M: HC+SS-FrM-7, **2**

Blair, R: HC+SS-FrM-9, **2**

— C —

Castegnaro, M: HC+SS-FrM-5, **1**

Chagoya, K: HC+SS-FrM-9, **2**

— D —

Deenen, C: HC+SS-FrM-2, **1**

— E —

Eads, C: HC+SS-FrM-6, **2**

Enes da Silva, M: HC+SS-FrM-1, **1**

Eyövge, C: HC+SS-FrM-2, **1**

— F —

Faria, J: HC+SS-FrM-1, **1**

— G —

Gardeniers, H: HC+SS-FrM-1, **1**; HC+SS-FrM-
2, **1**

— J —

Jiang, T: HC+SS-FrM-9, **2**

— K —

Kelber, J: HC+SS-FrM-6, **2**

— L —

Le, D: HC+SS-FrM-9, **2**

Lee, V: HC+SS-FrM-6, **2**

Lima, D: HC+SS-FrM-5, **1**

— M —

Mark, L: HC+SS-FrM-6, **2**

Medlin, J: HC+SS-FrM-6, **2**

Morais, J: HC+SS-FrM-5, **1**

— N —

Nash, D: HC+SS-FrM-9, **2**

— R —

Rahman, T: HC+SS-FrM-9, **2**

Rodriguez Olguin, M: HC+SS-FrM-1, **1**

— S —

Stacchiola, D: HC+SS-FrM-6, **2**

Susarrey Arce, A: HC+SS-FrM-1, **1**

Susarrey-Arce, A: HC+SS-FrM-2, **1**

— T —

Tenney, S: HC+SS-FrM-6, **2**

— W —

Wang, M: HC+SS-FrM-6, **2**

— Y —

Yano, J: HC+SS-FrM-3, **1**