

Tuesday Afternoon, October 29, 2013

Nanometer-scale Science and Technology
Room: 203 B - Session NS+AS+EN+SS-TuA

Nanoscale Catalysis and Surface Chemistry
Moderator: J. Nogami, University of Toronto, Canada

2:00pm **NS+AS+EN+SS-TuA1 Scanning Tunneling Microscopy Analysis of Molybdenum Sulfide Structures**, *C.S. Wang, W. Lu*, University of California, Riverside

Already commonly used industrially in the hydrodesulfurization process, MoS₂ is a promising catalyst that can exist as a stable monolayer film, much like graphene. This poster describes a method for growing MoS₂ monolayers on a copper substrate at a relatively low temperature and under mild sulfuration conditions through the use of thiophenol. Additionally, this procedure yields other molybdenum sulfide structures, including Mo₂S₃ films and Mo₆S₆ nanowires. To analyze the catalytic activity of these structures, we titrate using anthraquinone and formic acid as test molecules, thus determining the relative affinities for adsorbate interactions.

2:20pm **NS+AS+EN+SS-TuA2 Nanostructures of Au on Pd₃Fe(111) and Their Role in Electrochemical Oxygen Reduction**, *X. Yang*, Princeton University, *J. Hu, R.Q. Wu*, University of California, Irvine, *B. Koel*, Princeton University

Sluggish kinetics of the electrochemical reduction of molecular oxygen (ORR) in polymer electrolyte membrane fuel cells (PEM-FCs) requires a continued search for advanced catalysts. Our work combines synthesis and characterization of well-defined, multimetallic model catalysts in UHV and direct evaluation of their catalytic performance in an electrochemical cell accessible by a multifunctional ambient-pressure antechamber and sample transfer system. Surface structures and electronic properties [E] [E] of these electrocatalysts were characterized by LEED, AES, LEIS, XPS, and STM. We found previously that Pd₃Fe(111) annealed at high temperature is highly active for ORR, but may lose activity due to slow dissolution of Fe. To address this issue, we developed a method to improve the stability while maintaining high activity of the catalyst involving a submonolayer amount of Au at the surface. While bulk gold is catalytically inactive, the surface prepared by submonolayer amounts of Au deposited on a Pd/Pd₃Fe(111) substrate was discovered to be highly active for the ORR, more active than Pt(111). The activity was strongly dependent on the Au coverage, with the highest activity found near 0.5-monolayer Au. The high activity and durability of this Au-modified Pd₃Fe(111) surface is associated with formation of 2D nanostructures at the step edges at the surface, small nano-islands, which were revealed by STM. DFT calculations of O₂ adsorption on these 2D Au islands and of Au diffusion barriers to the top of Au terraces with and without O and O₂ were used to provide a more thorough understanding of the origin of the high catalytic activity of this system. We found that adsorbed oxygen atoms can enhance diffusion in Au protrusions, resulting in a 3D Au nanostructure that can lead to O₂ dissociation. In this work, we not only discovered a potential candidate for non-Pt catalysts to replace Pt cathode catalysts for the ORR, but also identified conditions for activating gold for use in practical electrocatalysts.

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2:40pm **NS+AS+EN+SS-TuA3 Oxygen Adsorption and Dissociation on Ag(110) and Au-Ag(110) Surfaces**, *M. Schmid, J. Klobas, R.J. Madix, C.M. Friend*, Harvard University

We have investigated the adsorption and dissociation of molecular oxygen on thin film Au-Ag alloys because of their potential for selective oxidation catalysis. Our work is motivated by an interest in fundamental understanding of nanoporous gold catalysts, which are a dilute Au-Ag alloy, typically containing 3-10% Ag; nevertheless, this dilute alloy is active for O₂ dissociation and for selective oxidation of CO and primary alcohols. We selected pure Ag(110) as a starting material because it strongly binds O₂ by donation of substantial charge density into the O=O bond. This species undergoes competing desorption of O₂ and dissociation to O atoms on the surface at ~170 K. We have investigated the effects of alloying with gold on the bonding and activity of O₂ using a combination of Scanning Tunneling Microscopy (STM), Temperature Programmed Reaction Spectroscopy (TPRS), and X-ray Photoelectron Spectroscopy (XPS). There is a rich morphology that develops on the surface depending on the Au content, and a substantially different reactivity towards oxygen as compared to pure Ag and Au substrates. Further investigations of selective oxidation processes on this surface are also planned.

3:00pm **NS+AS+EN+SS-TuA4 Trends in Reactivity of Organic Compounds on a Model Gold Catalyst**, *J.C. Rodriguez-Reyes*, Universidad de Ingeniería y Tecnología, UTEC, Peru, *C.M. Friend, R.J. Madix*, Harvard University

The perception that gold is chemically inert has faded in the light of the unique properties of this metal as an environmentally friendly catalyst. To date, the contrast between the large number of gold-based catalysts reported and the very limited number of probe molecules employed to test their efficiency has hindered the possibility of using gold beyond the laboratory scale and into an industrial scale as a practical catalyst. In this presentation, our efforts towards the elucidation of a reactivity scale for various organic molecules (including alcohols, amines, hydrocarbons, carboxylic acids and thiols) are discussed. The use of controlled (ultra-high vacuum) conditions allows for an assessment of the intrinsic behavior of gold as catalyst, with the mass spectrometric detection of desorbing products allowing both the identification of reactive species and the extraction of thermodynamics and kinetics parameters of importance for future studies. The results confirm that the first steps in gold-mediated reactions involve the dehydrogenation of a probe molecule and, therefore, there is a relationship between the gas-phase acidity of a molecule and its reactivity on gold. However, this relationship is modified by several factors including 1) the strength of the interaction of a functional group with the gold surface, 2) the presence of aromatic groups and long alkyl chains within a molecule, and 3) the presence of substituents able to modify the first two factors. The elucidation of a reactivity scale is anticipated to expand and direct the range of gold-mediated catalytic conversions.

4:40pm **NS+AS+EN+SS-TuA9 Single Atom Alloys as a Strategy for Selective Heterogeneous Hydrogenations**, *E.C.H. Sykes*, Tufts University
Hydrogenation reactions are central to the petrochemical, fine chemical, pharmaceutical, and food industries and are of increasing interest in energy production and storage technologies. Typical heterogeneous catalysts often involve noble metals and alloys based on platinum, palladium, rhodium and ruthenium. While these metals are active at modest temperature and pressure, they are not always completely selective and are expensive. We have demonstrated that single palladium atoms can convert the otherwise catalytically inert surface of an inexpensive metal into an ultrasensitive catalyst. We used high resolution imaging to characterize the active sites and temperature programmed reaction spectroscopy to probe the chemistry. The mechanism involves facile dissociation of molecular hydrogen at individual palladium atoms followed by spillover onto the copper surface, where ultrasensitive catalysis occurs by virtue of weak binding. The reaction selectivity is in fact much higher than that measured on palladium alone, illustrating the unique synergy of the system.

5:00pm **NS+AS+EN+SS-TuA10 Thin Film Synthesis and Oxidation: From C₆₀ and W Precursors to Intercalation, Nanospheres and Carbides**, *J. McClimon, P. Reinke*, University of Virginia

Tungsten carbide has garnered considerable interest for its catalytic activity and it is uniquely suited as an electrode/catalyst in microbial fuel cells. One of the bottlenecks in the use of W-carbide materials is their susceptibility to oxidation and concomitant loss in activity, albeit some surface processes benefit from the presence of surface oxide. The challenge is to establish the optimum oxide-carbide composition for a specific reaction and to stabilize this surface.

The W-carbide layers are synthesized from C₆₀ and W, which are deposited MgO(001) by electron and beam and thermal evaporation. This affords control of film composition, and lead us to an in-depth study of W-C₆₀ interaction, and discovery of a unique carbide nanosphere phase. The experiments are performed in UHV, and film growth and reactivity are studied with Scanning Tunneling Microscopy (STM) and Spectroscopy (STS), which delivers conductivity maps illustrating the progression of oxidation and variation in surface electronic structure.

Our work includes study of C₆₀-W interaction and carbide thin film growth using deposition of C₆₀ on W and vice versa, and co-deposition between 300-1000 K, and the study of oxidation of carbide films with a C/W ratio between 50/50 and 75/50, spanning the range from the line compound WC to carbon enriched films. The W/C 75/50 films have distinct graphite layers at the surface, while the W/C 60/40 surface presents mostly graphene patches. We will discuss the formation of carbide films, which retain some granularity defined by the C₆₀ molecule, in terms of thermodynamic and kinetic limitations. The progression of oxidation on the bare carbide surface, and competition with graphite/graphene etching define the overall reactivity. Conductivity maps yield a nano-scale view of the oxidation reaction as a function of temperature and p(O₂), which will be presented in the framework of a preliminary model.

We focus the discussion of W-C₆₀ interaction on the two major discoveries: (1) the intercalation of W into the C₆₀ matrix, and (2) the formation of carbide nanospheres.

The deposition of W on C₆₀ leads to the intercalation of W, and the cessation of molecule rotation due to the formation of W-C₆₀ complexes. The formation of exohedrally W-doped C₆₀ is described by a competition between complex formation and W-cluster growth. The inverted experiment, where C₆₀ is deposited on a W-surface and annealed at 600 (700)K leads to formation of carbide nanospheres, which are highly ordered with a narrow size distribution centered at 1.3 nm diameter. These nanospheres are metallic, and presumably form through the reaction between W and C₆₀, which acts as scaffold.

5:20pm NS+AS+EN+SS-TuA11 Selective Growth of TiO₂ Nanotubes on Titanium Foil by Two Step Anodization Method, Z. Razavi Hesabi, N. Semenikhin, A. Boncutter, F. Alamgir, E.M. Vogel, Georgia Institute of Technology, N.K. Allam, The American University in Cairo, Egypt

One dimensional nanostructures such as nanotubes exhibit unique properties because of their special geometry, high surface area and high aspect ratio paving the way for transferring ions, electrons, photons, gases, and fluids. The photoactivity of TiO₂ nanotubes (TNTs) makes them promising candidates for use in solar cells, water splitting, sensors, tissue engineering, and drug delivery. Among different synthesis methods, particular interest has been given to the anodic growth of TiO₂ nanotubes on Ti foil as it leads to the formation of an array of closely packed vertically aligned tubes. However, in many applications such as MEMS and NEMS, it is desired to have TiO₂ nanotubes with a desired pattern on substrate of interest. Pittrof et al. [1] patterned grown TiO₂ nanotubes after the nanotube layer has been created. Recently, Chappanda et al. [2] deposited Ti on silicon substrate and grew patterned TiO₂ nanotubes. Selective growth of TiO₂ nanotubes on titanium foil has not ever been reported. In the present study, TiO₂ nanotubes were grown selectively on patterned titanium foil by anodization at room temperature. Conventional photolithography as well as laser patterning of scotch tape were used to copy desirable pattern on titanium foil. Anodization was done in an organic electrolyte containing ammonium fluoride for 5 to 60 minutes. SEM images show successful growth of TiO₂ nanotubes in open areas.

1. A. Pittrof et al., *Acta Biomaterialia* **7** (2011)
2. K. N. Chappanda et al., *Nanotechnology* **23** (2012)

5:40pm NS+AS+EN+SS-TuA12 Process to Functionalize Polyaniline for Avidin-Biotin Biosensing Applications, T. Shaw, Clark Atlanta University, M.D. Williams, Clark Atlanta University, J. Reed, Clark Atlanta University

Biotin-avidin technology is a widely explored interaction in bioscience. Biotin's affinity for the protein avidin, makes it ideal for protein and nucleic acid detection or purification methods. This strong interaction is often used in pretargeting strategies for cancer treatment. In most cases a probe molecule (antibody) is connected to a marker molecule (fluorophore or nanoparticle) through the biotin-avidin bridge. Biotinylated nanoparticles can play a role in improving this interaction and creating an electronic or optical detection method. Polyaniline is a polymer which can be easily functionalized to be specific for various biomolecules and has ideal sensor characteristics. In this study we will design a process to functionalize polyaniline with biotin to create a biotin-avidin biosensor. We began with a 2-aminophenol which is a hydroxyl substituted aniline monomer. This monomer undergoes polymerization to yield 2-hydroxy polyaniline. The polymer's hydroxyl group was functionalized by Steglich esterification which refluxes a carboxylic acid with an alcohol. This esterification drives the reaction and dehydrates the products shifting the equilibrium towards the product. In this reaction DCC (dicyclohexylcarbodiimide) activates the carboxylic acid of biotin to further reaction and DMAP (4-dimethylaminopyridine) acts as the acyl transfer catalyst. The biotinylated polyaniline derivative was characterized using FT-IR spectroscopy, ¹H NMR spectroscopy, UV-VIS spectroscopy, and Scanning Electron Microscopy.

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