

Wednesday Afternoon, October 21, 2015

Nanometer-scale Science and Technology

Room: 212B - Session NS+EN+MG+SS+TF-WeA

Nanoscale Catalysis and Surface Chemistry

Moderator: Sidney Cohen, Weizmann Institute of Science, Israel

2:20pm NS+EN+MG+SS+TF-WeA1 Effects of γ -Al₂O₃ Support on the Geometry and Electronic Structure of H-covered Pt Nanoparticles, *Sampyo Hong, G. Shafai, T.S. Rahman*, University of Central Florida

We have studied the effects of γ -Al₂O₃(110) support on the geometry and electronic structures of H-covered Pt_x (x=22,44) nanoparticles (NP) using density functional theory (DFT). We find that the unoccupied d-band center of γ -Al₂O₃(110) supported Pt NPs exhibits a blue shift with decreasing Pt size similarly as the measured XANES absorption peak energy of Pt NP samples. In fact, our DFT results reveal that the shift of the unoccupied d-band center of Pt NPs is dependent of surface hydroxylation level on γ -Al₂O₃(110). At higher hydroxylation the calculated unoccupied d-band center can even show red shift. Thus, consideration of hydroxylation level on γ -Al₂O₃(110) is needed to properly interpret support effect from XANES spectra. Overall, the strength of Pt- γ -Al₂O₃(110) binding seems to be a reasonable measure of the shift of unoccupied d-band center as a result of metal-support interaction: the stronger the interaction the more the blue shift. In the light of these results, it is plausible to postulate that the adsorption energy shift of XANES spectra represent the strength of metal-support interaction (support effect). A remarkable example of such hydroxylation tuned metal-support interaction is structural transition of Pt₂₂ from a biplanar to a 3D-like geometry as a function of support hydroxylation.

This work is supported in part by DOE Grant DE-FG02-07ER15842.

3:00pm NS+EN+MG+SS+TF-WeA3 Fabrication and SERS Activity of Metal-loaded TiO₂ Nanometer Scale Particles, *Paolo Reyes, J.C. Hemminger*, University of California Irvine

Our current research focuses on the fabrication and study of metallic loaded titanium dioxide (TiO₂) nanoparticles supported by highly oriented pyrolytic graphite (HOPG). Highly dispersed TiO₂ particles are formed via physical vapor deposition (PVD) under high vacuum settings with an average pseudo-diameter of 11.6 ± 2.65 nm. Metallic loading is completed by an ex-situ photo-deposition method by exposure to precursor metal salt solutions under TiO₂ bandgap UV irradiation. We have attempted to fabricate Pt-, Ag-, Au-, and Pt-Au-TiO₂ particles and observed photocatalytic enhancement with the inclusion of Pt nanoparticles deposited onto TiO₂ surfaces. We believe this enhancement is a result of Pt nanoparticles harboring free excited electrons and preventing electron-hole recombination. We have developed a technique to increase the density of TiO₂ particles by creating site defects on the surface of HOPG through plasma mild oxygen plasma exposure. Highly dispersed TiO₂ nanoparticle distributions allow an increase of metal nanoparticle formation on TiO₂ for surface and intrinsic property observations. Ag nanoparticles have been fabricated in order to observe Surface Enhanced Raman Spectroscopy (SERS) Ag nanoparticles were observed to be an average pseudo-diameter of 2.6 ± 1.4 nm. A probe molecule was used to determine Raman intensity enhancement factor (EF) and we believe that the EF can be affected by the spacing and size of Ag-TiO₂ nanoparticles. We will present our studies of bi-metallic loading of TiO₂.

This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences through grant number: DE-FG02-96ER45576

4:20pm NS+EN+MG+SS+TF-WeA7 Pyridine Coordination Chemistry for Molecular Assemblies, *Milko Van der Boom*, Weizmann Institute of Science, Israel **INVITED**

Many types of metal-ligand interactions have creatively been used in the chemical sciences since the description of coordination complexes. The rich coordination chemistry of pyridine-type ligands has contributed significantly to the incorporation of metal ions into functional materials on surfaces. We will discuss molecular assemblies formed with a variety of pyridine-based compounds. These assemblies are formed by layer-by-layer deposition from solution that allows for precise fitting of the assembly properties. The degree of intermolecular interactions can be controlled by varying the degree of π -conjugation and the availability of coordination sites. Unlike molecular assemblies that are constructed with organic ligands, assemblies with polypyridyl complexes are active participants in their own

formation and amplify the growth of the incoming molecular layers. Such a self-propagating behavior for molecular systems is rare and the mechanism of their formation will be presented. Incorporating multiple metal complexes into a single assembly give rise to composite materials that exhibit unique electrochemical and electrochromic properties that are dependent on the arrangement of these metal complexes. We will also discuss the coordination chemistry of pyridine-based compounds with nanoparticles, the formation of metal-organic frameworks and their practical applications.

5:00pm NS+EN+MG+SS+TF-WeA9 Atomic Scale Iron Carbide Films on Au(111) and Cu(111) as a Iron Fischer-Tropsch Model Catalyst, *Gilbère Mannie, X. Wen, Y.W. Li*, SynCat@Beijing, China, *J.V. Lauritsen*, Interdisciplinary Nanoscience Center (iNANO), Denmark, *H.J.W. Niemantsverdriet*, SynCat@Beijing, China

Iron-based Fischer-Tropsch synthesis (FTS) is one of the most investigated catalytic systems in the world due to the ability to convert any form of hydrocarbons like coal, natural gas or biomass into diesel, gasoline and chemicals [1]. Although investigated for more than 50+ years, fundamental surface reactions involved in this process are not known or fully understood. Within the FTS community, iron carbide is seen as the active phase in the catalytic process but the atomic-scale surface structure and even the stoichiometry of the bulk phase is a matter of debate [1,2]. In order to fundamentally investigate the active phase, to for example verify molecular modeling studies on iron carbide surfaces (like [3,4]), we successfully synthesized highly-crystalline iron carbide monolayer islands (on Au(111)) and multilayer islands (on Cu(111)). Obtained carbidic films are suitable for analysis with scanning tunneling microscopy (STM) and other surface science techniques. Our atomically-resolved STM results, together with preliminary density functional theory (DFT) results show that we can characterize our iron carbide (Fe_xC_y) islands as iron layer with interstitial carbon atoms, based on the increase of the inter-atomic Fe-Fe distance [5]. During the synthesis of the Fe_xC_y islands we were able to record some STM movies showing the formation of the carbidic phase out of the metallic phase but we could also record movies during dosing experiments of several gasses (H₂, O₂) to the pure iron carbide islands. During the presentation we will explain how we synthesized these crystalline iron carbide films and how these films can act as a model system for fundamental Fischer-Tropsch catalyst research.

[1] E. de Smit, B. M. Weckhuysen, *Chem. Soc. Rev.*, **2008**, *37*, 2758

[2] J. W. Niemantsverdriet, A. M. van der Kraan, W. L. van Dijk, H. S. van der Baan, *J. Phys.*, **1980**, *84*, 3363

[3] J. M. Gracia, F. F. Prinsloo, J. W. Niemantsverdriet, *Catal. Lett.*, **2009**, *133*, 257

[4] M. O. Ozbek, J. W. Niemantsverdriet, *J. Catal.*, **2014**, *317*, 158

[5] G. J. A. Mannie, L. Lammich, Y. W. Li, J. W. Niemantsverdriet, J. V. Lauritsen, *ACS Catal.*, **2014**, *4*, 3255

5:20pm NS+EN+MG+SS+TF-WeA10 Fullerene Interaction with W Surfaces: Synthesis of Nanospheres with Tunable Bandgap, *Ehsan Monazami*, University of Virginia, *J.B. McClimon*, University of Pennsylvania, *P. Reinke*, University of Virginia

The interaction of f C₆₀ molecules with metal surfaces is a topic of considerable interest and discussed in the context of molecular electronics and organic solar cell applications. Our work focuses on the interaction of C₆₀ with W, which is a carbide forming transition metal. It has generally been assumed that the C₆₀ cage breaks up readily on a W surface, but our observations reveal a more complex, temperature induced reaction sequence leading to the formation of nanospheres with variable bandgap, which has been studied with in-situ STM and STS analysis.

The nanospheres are synthesized by initiating the reaction between C₆₀ deposited on a W-thin film surface grown on MgO(001) at about 450 K. In contrast to previous reports, the molecules do not collapse but the spherical shape is retained up to 800 K and the electronic structure changes gradually from wide bandgap C₆₀ to fully metallic nanospheres. The size distribution of the nanospheres is centered at 1.5 nm (600 K) and shifts for higher temperatures to about 2 nm with a concurrent decrease in height resulting in an ellipsoidal shape. These nanospheres present an exceptional resistance to sintering which is a unique feature for metallic nanoparticles. The densely packed C₆₀ and isolated C₆₀ molecules show the same transition in shape and electronic structure which confirms that the transformation is controlled by the reaction with the W substrate.

The transition in the electronic structure progresses gradually from the wide-bandgap molecule (2.3 eV) to a bandgap of ~1eV at 700 K, and a metallic surface at 800 K. We will illustrate this progression with a series of

ST spectra and maps. The bandgap variation offers for the first time a pathway to the formation of nanoscale clusters (nanospheres) with variable bandgap while retaining the surface curvature in narrow range. The detailed structure of the nanospheres is, however, still subject to discussion. We currently favor, based on our experimental results, a substitution model where the W-atoms from the substrate react with the C₆₀ cage which acts as a scaffold. The W atoms are incorporated substitutionally forming a carbide type bonding, whose presence is indicated by XPS analysis. The variation in bandgap is then driven by the degree of substitution and the fullerene molecule acts as a scaffold. We predict that other carbon scaffolds such as nanotubes and carbide forming transition metals can react in the same manner leading to a new class of nanostructures with unique adaptability of the electronic structure. The nanospheres are an excellent testbed for the physics and chemistry of highly curved surfaces.

Supported by NSF-DMR Ceramics DMR-100580.

5:40pm **NS+EN+MG+SS+TF-WeA11 Enantiomeric Separations of Chiral Pharmaceuticals using Chiral Tetrahedral Au Nanoparticles**, *Nisha Shukla, D. Yang, A.J. Gellman*, Carnegie Mellon University

Chiral tetrahedral (24-sided) Au nanoparticles are tested for their use as chiral separators of pharmaceutical drugs in solution phase. Tetrahedral Au nanoparticles were chirally modified with either D- or L-cysteine. They show enantioselective adsorption of pharmaceuticals such as propranolol hydrochloride (used for anxiety and high blood pressure) from a solution of racemic propranolol hydrochloride, thus leaving an enantiomeric excess in the solution phase. This work suggests that chiral nanoparticles can be used for enantiomeric separation of real pharmaceutical drugs. A simple robust model has also been developed that allows extraction of the enantiospecific equilibrium constants for R- and S-propranolol hydrochloride adsorption on the chiral tetrahedral Au nanoparticles. The model obviates the need for experimental determination of the surface area of absorbent Au nanoparticles which is extremely difficult to measure.

6:00pm **NS+EN+MG+SS+TF-WeA12 Electroreduction Catalysis with Defect-Rich Metal Nanoparticles**, *Xiaofeng Feng, M. Kanan*, Stanford University

New design principles for electroreduction catalysts are essential for CO₂ recycling using renewable electricity. Au is one of the most active catalysts for CO₂ reduction to CO, and numerous efforts have been made to optimize Au catalysts by tuning the size, composition, and shape of Au nanostructures. Here we show that grain boundaries (GBs) in Au nanoparticles create highly active surface sites for CO₂ electroreduction (1). Defect-rich Au nanoparticles were synthesized by vapor deposition of Au onto a carbon nanotube thin film, which enables direct TEM characterization without further processing. We compared the CO₂ reduction activity of the as-deposited catalysts to those annealed at different temperatures. While the annealing process has little impact on the distribution of Au surface facets, it reduces the GB density, which is quantified by measuring GB lengths and particle areas from high-resolution TEM images. We found that the surface-area-normalized activity for CO₂ reduction is linearly correlated with GB density in Au nanoparticles in the low overpotential regime. Similarly, GB-density was also found to correlate with catalytic activity for the electroreduction of CO to multi-carbon oxygenates on Cu nanoparticles. Our studies show that grain boundary engineering is a general strategy for improving electrocatalytic activity for carbon fuel synthesis.

References:

(1) Feng, X.; Jiang, K.; Fan, S.; Kanan, M. W. *J. Am. Chem. Soc.* **2015**, *137*, 4606–4609.

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