

## Nanomaterials

Room: Hau - Session NM-MoE

### Nanomaterials Characterization & Reactivity I

Moderator: Takhee Lee, Seoul National University

5:40pm **NM-MoE1 Interfacial Chemistry between gas-phase molecules and GaAs surfaces: morphology dependence**, *Sylvia Ptasinska, XQ. Zhang*, University of Notre Dame

A detailed understanding of molecular interactions at the interface of two-dimensional GaAs systems under ultra-high vacuum (UHV) conditions has been achieved over the decades. While research on the understanding of such interactions with lower-dimensional GaAs-based structures, such as one-dimensional nanowires (NWs), has not been performed despite the potential importance of these structures in developing nano-electronic devices. Moreover, surface characterization of GaAs under more realistic conditions rather than the UHV studies, are critical in any attempt to correlate surface chemistry with device properties.

Due to recent advances in the surface characterization techniques, and especially the development of Near Ambient Pressure X-ray Photoelectron Spectroscopy (NAP XPS) [1], we are able to monitor in-situ surface chemistry under elevated pressures and temperatures.

In our present work, we performed NAP XPS studies for different GaAs morphologies:

the simple planar GaAs(100) crystal and a radically non-planar GaAs surface comprised of an ensemble of GaAs NWs under elevated pressures of O<sub>2</sub> or H<sub>2</sub>O molecules. The evolution of O<sub>2</sub> and H<sub>2</sub>O molecule dissociation on GaAs NWs was tracked under in-situ conditions as a function of temperature and gas pressure to establish whether the processes of dissociation leading to oxidation an hydroxylation depend on surface morphology. In contrast to ideally flat GaAs single crystal surfaces [2], gas molecules experienced the enhanced dissociation on GaAs NW ensembles due to an increase in the surface area ratio and the presence of stepped edges, atom vacancies, and other defects on non-flat semiconductor surfaces [3].

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6:00pm **NM-MoE2 Reactivity of Hydrogen-Absorbed Pd and PdAu Alloy Surfaces**, *S. Ohno, S. Ogura, M. Wilde, Katsuyuki Fukutani*, University of Tokyo, Japan

Pd is a typical material that absorbs hydrogen in its bulk, and hydrogen absorbed in Pd clusters was shown to play an essential role in olefin hydrogenation reactions [1,2]. We have recently studied absorption of hydrogen in Pd(110) [3] and Pd<sub>70</sub>Au<sub>30</sub>(110) [4], and shown that hydrogen can be efficiently absorbed in Pd<sub>70</sub>Au<sub>30</sub>(110) [4]. In the present work, we have studied reactivity of Pd(110) and Pd<sub>70</sub>Au<sub>30</sub>(110) alloy surfaces towards olefin hydrogenation reactions with thermal desorption spectroscopy (TDS) and nuclear reaction analysis (NRA) that allows for high-resolution depth profiling of hydrogen [5].

When a Pd(110) surface was exposed to H<sub>2</sub> at a low temperature, TDS revealed desorption features at ~150 K and ~300 K, which are attributed to hydrogen absorbed in the bulk and adsorbed on the surface, respectively [3]. Whereas coadsorption of C<sub>4</sub>H<sub>8</sub> with surface H on Pd(110) revealed no hydrogenation reaction, hydrogenated products of C<sub>4</sub>H<sub>10</sub> were clearly observed in presence of H in the adsorbed state. When the Pd<sub>70</sub>Au<sub>30</sub>(110) surface was exposed to H<sub>2</sub>, on the other hand, a single desorption feature was recognized at ~250 K, which is different from both the pure Pd(110) and Au(110) surfaces [4]. Examination of the Pd<sub>70</sub>Au<sub>30</sub>(110) surface with low-energy electron diffraction and Auger electron spectroscopy revealed that Au segregates at the surface of the alloy. Hydrogen is dissociated at

minor Pd sites on the surface and absorbed into bulk through the Pd site without spillover onto the Au site [4]. When C<sub>4</sub>H<sub>8</sub> was adsorbed on the D-adsorbed Pd<sub>70</sub>Au<sub>30</sub>(110) surface, TDS showed no hydrogenated products of C<sub>4</sub>H<sub>10</sub>, which is in remarkable contrast with the Pd(110) surface. Instead of the hydrogenation reaction, H-D exchange reactions were clearly observed. We discuss the reaction mechanisms on these two surfaces.

#### References

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- 2) M. Wilde et al., *Ang. Chem. Int. Ed.* 47 (2008) 9289.
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- 5) K. Fukutani, *Curr. Opin. Sol. Stat. Mater. Sci.* 6 (2002) 153.

6:20pm **NM-MoE3 Alumina Incorporated Tin Oxide (SnO<sub>2</sub>) Pellets as Co Sensors**, *O. Amador, Cinvestav-Ipn*, Mexico City, Mexico, *Krishnakarthik Venkata, A. Maldonado*, Cinvestav- Ipn, Mexico City, Mexico

In this work we have utilized a novel Chemical-physical method for synthesis of SnO<sub>2</sub> nanoparticles. In two previous works [1,2], we have reported about the homogeneous precipitation synthesis of SnO<sub>2</sub> powders by two different precipitation agents, Urea and Ammonia; those powders were further ball milled to manufacture SnO<sub>2</sub> pellets and then tested for CO gas sensing. Compared to other methods [3-4] our synthesis route offers SnO<sub>2</sub> particles with very less agglomeration, particle size in the order of 15-20 nm, and homogeneous size distribution of the particles. An research group reported a maximum sensitivity for SnO<sub>2</sub> pellets around 8, for 1000 ppm of CO at operating temperatures of 300°C [5], whereas in our pellets, sensitivities were around 300 and 550 for CO when were measured at 300 ppm for 200and 300°C, respectively. Later the ball milled powders were mixed with Al<sub>2</sub>O<sub>3</sub> powders (particle size around 1µm) with different ratios like 1:1, 2:1 and 4:1 in order to save tin oxide powder and also for increasing the oxygen trapping by increasing the porosity of the pellets. The effect of alumina mixing ratio on the pellets sensitivity was also studied. Maximum sensitivity obtained in pellets manufactured from ball milled SnO<sub>2</sub> powders, at 300 °C for 300 ppm, by two different powder preparation routes were **548** and **262**, whereas for mixing pellets with alumina at a 2:1 ratio (SnO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub>), were **483** and **340**, for the same two preparation methods. The tendency of increasing the sensitivity with the operation temperature and the gas concentration was achieved successfully. The sensitivities obtained for pure ball milled SnO<sub>2</sub> and alumina 2:1 mixed pellets were almost in the same range. Therefore, high sensitivities can be achieved with less sensing material.

**Keywords:** Gas Sensors; Homogenous Precipitation; Sensitivity; CO, Pellets; Tin Oxide Powders.

#### References:

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6:40pm **NM-MoE4 Nanocatalysts at Work**, *Beatriz Roldan Cuenya*, Ruhr University Bochum, Germany **INVITED**

In order to comprehend the properties affecting the catalytic performance of metal nanoparticles, their dynamic nature and response to the environment must be taken into consideration. The working state of a nanoparticle catalyst might not be the state in which the catalyst was prepared, but a structural and/or chemical isomer that adapted to the particular reaction conditions. This work provides examples of recent advances in the preparation and characterization of nanoparticle catalysts with well-defined sizes and shapes. It discusses how to resolve the shape of nm-sized Pt, Au, Pd, Cu, and PtNi catalysts via a combination of *in situ* microscopy (AFM, STM, TEM), *operando* spectroscopy (XAFS, GISAXS) and modeling, and how to follow its evolution under different gaseous or liquid chemical environments and in the course of a reaction. It will be highlighted that for

structure-sensitive reactions, catalytic properties such as the reaction rates, onset reaction temperature, activity, selectivity and stability against sintering can be tuned through controlled synthesis. Examples of catalytic processes which will be discussed include the gas-phase oxidation of alcohols (methanol and butanol), the oxidation of NO, and the electrochemical reduction of CO<sub>2</sub>. Emphasis will be given to elucidating the role of the nanoparticle size, shape, and chemical state in the activity and selectivity of the former reactions.

7:40pm **NM-MoE7 Surface Chemistry of Environmentally and Biologically Relevant Molecules on Nanoparticle Surfaces**, *Vicki Grassian*, University of Iowa, USA **INVITED**

The adsorption of environmentally and biologically relevant molecules on the surface of metal oxide nanoparticles can impact the properties of these small particles and thus their behavior. In particular, the impact of surface adsorption of environmentally and biologically relevant molecules from the gas and liquid phase on the properties of nanoparticles in aqueous suspensions (dissolution, aggregation and reaction chemistry) will be presented. Additionally, the role of size, particularly for nanoparticles below 10 nm in diameter, will be discussed. The approach in these studies is to combine nanomaterial characterization using a wide range of techniques including microscopy, spectroscopy, light scattering measurements, along with molecular probes of surface adsorption and surface chemistry to better understand the behavior of oxide nanomaterials in the presence of environmentally and biologically relevant ligands.

8:20pm **NM-MoE9 Novel Fabrication of Titanium Dioxide Nanotubes for Cancer Photothermal Therapy**, *W. Srituravanich*, Department of Mechanical Engineering, Chulalongkorn University, Thailand, *Bunlaporn Thumrongthanyaluk*, International School of Engineering, Chulalongkorn University, Thailand

Titanium dioxide nanotubes (TiO<sub>2</sub> NTs) have attracted significant attention in biomedical applications due to their biocompatibility and photocatalytic properties. Such a nanomaterial can be coupled with near-infrared irradiation to heat bio-molecules such as cancer cells causing them to death so-called cancer photothermal therapy. In this work, we proposed a novel method to fabricate isolated TiO<sub>2</sub> NTs and utilized them as a therapeutic agent in cancer photothermal therapy. TiO<sub>2</sub> NTs were synthesized by anodization of titanium electrode using diethylene glycol (DEG) +2 vol% HF as electrolyte. TiO<sub>2</sub> NTs were then isolated from Ti substrate by sonication in isopropanol (IPA) for 20 mins. The hepatic cancerous cells (HepG2) were treated with different concentrations of isolated TiO<sub>2</sub> NTs; 0, 6.25, 12.5 and 25 mg/ml under three exposure conditions; dark (no irradiation), UV and Near-Infrared (NIR) irradiation. After the treatment, *in vitro* cell experiment was performed to measure the viability of the cells. According to the results, the viability of cells under NIR irradiation dropped with the increment of the concentration of TiO<sub>2</sub> NTs. At the concentration of 25 mg/ml the viability was reduced by 31%. Thus, isolated TiO<sub>2</sub> NTs shows promising results for cancer photothermal therapy.

8:40pm **NM-MoE10 Surface Chemistry of Ore-Binder Mixture System in Relation to Iron Ore Pelletisation**, *Akira Otsuki*, University of Lorraine, France

The surface property of single and multi-minerals (hematite and gangue) with bentonite

binder was investigated to produce quality pellets by properly controlling the surface properties of

minerals and to beneficiate low grade/fine iron ores. The results showed that zeta potential of

hematite-bentonite mixture did not change with the bentonite dosage. On the other hand, the type and

amount of gangue minerals greatly affected the zeta potential of the mineral mixture with bentonite.

Specifically, the amount of silica presented in the system governed the changes in zeta potential due to

the bentonite adsorption on silica surface and its charge while alumina had no effect. This is due to

their nature of the charges and interaction with bentonite. This study indicated that the mineral

composition of iron ores significantly affected the surface charge of the ore, and can noticeably

influence the quality of pellets formed by iron ores with the binder.

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