Plasma Science and Technology Division
Room: 22 - Session PS+NS+SS-WeM

Plasma Processing for Nanomaterials & Nanoparticles
Moderators: Hisataka Hayashi, Toshiba, Japan, Kazunori Koga, Kyushu University, Japan

8:00am **PS+NS+SS-WeM1 Plasma Catalysis: a Powerful Blend of the Four States of Matter**, ***Kostya (Ken) Ostrikov***, Queensland University of Technology and CSIRO, Australia **INVITED**

Plasma catalysis is a rapidly emerging multidisciplinary field at the interface of catalysis, nanotechnology, physical chemistry, materials and plasma science. Relevant applications include plasma-assisted catalytic reforming of gas mixtures into fuels, chemicals and synthesis of functional nanomaterials. Plasma-specific effects play a major role in nanoscale catalytic phenomena. The process outcomes are improved when catalysts with nanometer-scale surface features are used along with atmospheric-pressure plasmas (APPs). It is possible that plasmas and catalysts act synergistically.

I will review the APP interactions with the nanometer-size features on the surface of catalyst nanoparticles (NPs). Basic understanding of plasma-catalyst interactions is achieved through nd the effects of these modified surfaces on catalytic reactions. Nanoscale interactions of APPs with the NPs and synergistic effects are related to plasma modifications of catalyst structure and reactivity. The synergistic effects may increase the yield and selectivity of catalytic reactions of importance to chemical and energy resource industries.

The focus is on gas mixtures relevant to natural reforming or hydrogen production by water splitting. The selected nanomaterials catalyze the conversion of the above gas mixtures into higher-value products such as synthetic gas (syngas), hydrogen, fuels, etc. of demand in a variety of industrial applications (e.g., methanol production). The plasmas induce "epigenetic" modifications of catalytic materials and the plasma process parameters are customized to maximize both the conversion rates and the process gas flow, i.e., both the outcome (selectivity) and the productivity (rates) of the gas conversion.

I will discuss the most effective nanoscale plasma-surface interactions. The focus will be on surface modifications (e.g., functionalization, expression of crystal facets, changes in reactivity of near-surface atoms, oxidation or reduction states, etc.) of localized surface areas induced by the nanoscale plasma-surface interactions and chemical reactions. The plasma effects enhance reactivity of the "epigenetically" modified surface areas of the NPs. The expected effects include better adsorption, higher conversion rates of reactant species on the modified surfaces, larger surface areas for reactions, higher catalytic activity through more effective electron transfer, reduced reaction activation barriers, photon- and ion-assisted reactions, new plasma-enabled reaction pathways, etc.

8:40am **PS+NS+SS-WeM3 Vaporization of Nanoparticles in Low Temperature Plasmas**, ***Necip Berker Uner***, *E. Thimsen*, Washington University in St. Louis

Particle nucleation is a major problem that occurs in many thin film processing plasmas. The resultant "killer particles" can create defects upon deposition on the film and they can consequently decrease device functionality. A change of perspective, within the last two decades, the aptness of low temperature plasmas (LTP) for particle nucleation has been successfully exploited to synthesize monodisperse, free standing, spherical and crystalline semiconductor nanocrystals from vapor precursors. These impressive properties of particles synthesized in LTPs stem from particle charging and ion bombardment. When the particle number density is smaller than the ion density, it is proposed that the particles experience unipolar charging. The negative charge acquired by the particles suppresses coagulation and leads to uniform growth. On the other hand, ion bombardment elevates particle temperatures above the surrounding gas temperature and provides crystallinity. By using LTPs, nanocrystals of silicon, germanium, various oxides, sulfides and compound semiconductors of high quality have been produced, whereas production of metal particles were less successful, which indicates incomplete understanding.

In this study, we focus on the interaction between the plasma and metal nanoparticles. In an environment free of vapor precursors, we demonstrate that particle growth in LTPs follows a reversible path. Instead of continuous growth, ion bombardment can lead to extensive vaporization, depending on the plasma density and vapor pressure. By sending in a premade aerosol of bismuth particles through a capacitively coupled radio frequency argon plasma, we observed complete vaporization of the metal at moderate power inputs. Interestingly, at low power inputs, vaporization resulted in significant restructuring of the particle size distribution. Polydispersed size distributions were transformed into monodispersed distributions, with relatively high mass yields reaching 65%. Based on spatial Langmuir probe measurements and detailed aerosol dynamics modelling, we propose that upon exposure to different plasma densities, particles can vaporize and then the resultant vapor can either nucleate into particles or recondense on the remaining clusters, eventually leading to the modification of the size distribution. When particles vaporize completely and the vapor is conserved, the result is the conversion of a polydispersed size distribution into a monodispersed size distribution. This unusual mechanism that involves vaporization at low temperature will be detailed with further experimental observations with different materials. Methods of tuning the final size will be elaborated.

9:00am **PS+NS+SS-WeM4 Nanowires, Trusses and Pillars Produced by Assembly of Plasma Generated Nanoparticles**, ***Ulf Helmersson***, *S. Ekeroth, S. Askari, R. Boyd, N. Brenning*, Linköping University, Sweden

Nanoparticles generated or supplied to a plasma attains a negative potential due to the nature of the plasma. This open up interesting possibilities in synthesis and assembly of the nanoparticles creating structures in the nano- and micro-range. In this work, we use hollow cathode sputtering powered with high-power pulse to ensure close to full ionized of the source material. This promotes rapid growth of the nanoparticles to desired sizes and the negative charge makes it possibility to guide nanoparticles for assembly and collection on desired positions. This is demonstrated by attracting nanoparticles to substrate positions with a positive potential and focusing nanoparticles through a matrix of electrostatic lenses to assemble the nanoparticles into pillars. For ferromagnetic nanoparticles, we also demonstrate generation of nanowires as well as nanowires cross-linked into trusses. Since the iron nanoparticles are generated under relatively pure condition they assemble into wires without oxides in the interfaces. Nanowires and trusses assembled on conducting substrates can potentially be used as low cost large area electrodes.

9:20am **PS+NS+SS-WeM5 Non-Equilibrium Plasmas for Nanoparticle Synthesis: from Semiconductors to Metals**, ***Rebecca Anthony***, Michigan State University **INVITED**

Nonthermal plasmas have been increasingly popular for synthesis of nanocrystals. Generally, these flow-through reactors are radiofrequency (RF) plasmas operated at reduced pressure (2-10 Torr) into which vapor-phase precursors are entrained. The nanocrystals form following dissociation and clustering of the precursor molecules. Among the advantages offered by plasma reactors are low-temperature environment, avoidance of liquid-phase reactants, tunable nanocrystal properties via reactor parameters, and scalability. In addition, the nanocrystals can be collected as powders for post-processing, or directly impacted onto substrates in thin-film form, sidestepping the need for additional steps such as spin- or drop-casting. Combined with the solvent-free, low-temperature, all-gas-phase nature of nonthermal plasma reactors, this opens the door to direct incorporation of nanocrystals into functional layers on arbitrary substrates - without concern about solvent orthogonality or thermal susceptibility.

Here we present our work focusing on exploiting the non-equilibrium of plasma reactors for high-quality nanocrystal growth. First we discuss silicon nanocrystals for optical applications. The properties of these nanocrystals, such as size, crystallinity, and surface, can be altered in-flight using the plasma reactor parameters - and they can be inertially impacted onto a variety of substrates. These nanocrystals exhibit efficient and tunable photoluminescence, and we have deployed them in LEDs, luminescent layers on stretchable substrates, and as sensitizers for pollutant photodegradation. The non-equilibrium environment of the plasma also allows growth of even higher-melting-point nanocrystals, and we will share our work on GaN nanocrystal growth using plasma reactors. These freestanding nanocrystals are size-tunable and have excellent crystal quality despite GaN having a bulk melting temperature of 2500°C. Finally, we will discuss formation of metal nanoparticles in the plasma using an altered-geometry RF plasma with a central consumable ground electrode, working towards expanding the range of optoelectronically functional nanomaterials that can be made using nonthermal plasmas.

11:00am **PS+NS+SS-WeM10 Photochemical Insulator-Metal Transition in Plasma-Synthesized ZnO Nanocrystal Networks**, ***Benjamin Greenberg***, *Z. Robinson, K. Reich*, University of Minnesota, *C. Gorynski*, University of Duisburg-Essen, Germany, *B. Voigt*, University of Minnesota, *G. Nelson*, Creighton University, *L. Francis, B. Shklovskii, E.S. Aydil, U.R. Kortshagen*, University of Minnesota

Nonthermal plasma synthesis has recently emerged as a promising method for producing highly conductive ZnO nanocrystal (NC) networks. The plasma-synthesized NC surfaces are free of ligands, which enables high interparticle electron mobility. In this work, we produce ZnO NC networks using nonthermal plasma synthesis integrated with supersonic inertial impaction deposition, and we manipulate their electron transport properties with a combination of UV illumination and NC surface modification via atomic layer deposition (ALD). Specifically, we use these treatments to increase the free electron density, n, and the interparticle contact radius, ρ, and thereby induce a transition from variable range hopping to metallic transport. We determine n from the NCs' localized surface plasmon resonance (LSPR) and ρ from the subtle increase in the ZnO volume fraction, and we use Fourier transform IR spectroscopy (FTIR) to ascertain the underlying NC surface photochemistry.

11:20am **PS+NS+SS-WeM11 Elucidating Energetic Trends in Hydrocarbon Plasma Systems for Plasma-Assisted Catalysis**, ***Tara Van Surksum***, *E.R. Fisher*, Colorado State University

Plasma-assisted catalysis (PAC) has been investigated as a promising method for pollution control, specifically for conversion or removal of volatile organic compounds. The utility of PAC is severely limited by an overall lack of understanding of plasma chemistry and the reactions occurring at the plasma-catalyst interface. The present work focuses on investigating fundamental gas-phase chemistry in hydrocarbon inductively-coupled plasma systems to understand energy partitioning in PAC systems for decomposition of volatile organic compounds. We have employed broadband absorption and optical emission spectroscopies to determine rotational and vibrational temperatures (T_R and T_V, respectively) for multiple species (e.g., CH, C_2) in a variety of hydrocarbon-containing plasma systems. For example, in CH_4 plasmas, T_V(CH) ranges from ~3000 to ~5000 K, whereas T_R(CH) generally reaches values ranging from 1000-2000 K. Energy partitioning for the same species has also been assessed when a catalytic material (e.g., flat and nanostructured SnO_2 and TiO_2, micro-structured zeolites) is placed in the plasma. In some cases, the substrate has a measureable effect on the gas-phase chemistry, whereas in others the substrate does not appreciably alter the gas-phase of the plasma. Catalytic material properties were also evaluated via surface analysis tools (e.g., X-ray photoelectron spectroscopy, scanning electron microscopy, and Fourier transform infrared spectroscopy) and will be presented in conjunction with energy partitioning data to further elucidate information on the molecular-level processes occurring at the plasma-catalyst interface. Collectively, these data aim to unravel the complex chemistry of hydrocarbon plasma systems for PAC to achieve a viable method of pollution control.

11:40am **PS+NS+SS-WeM12 Synthesis of Metal Nanoparticle Electrocatalysts for Fuel Cell Applications by Atmospheric-Pressure Plasma Reduction**, ***Joffrey Baneton****, Université Libre de Bruxelles, Belgium, *Y. Busby*, Université de Namur, Belgium, *W. Debouge*, Université Libre de Bruxelles, Belgium, *G. Caldarella*, Université de Liège, Belgium, *J.-J. Pireaux*, Université de Namur, Belgium, *V. Debaille*, Université Libre de Bruxelles, Belgium, *N. Job*, Université de Liège, Belgium, *M.J. Gordon*, University of California at Santa Barbara, *R.M. Sankaran*, Case Western Reserve University, *F. Reniers*, Université Libre de Bruxelles, Belgium

Nanoparticles composed of one or more metals particularly platinum (Pt) are used as electrocatalysts in hydrogen fuel cells for the cathodic reduction of dioxygen [1]. Several challenges remain in their synthesis including controlling their morphological features (e.g. size, shape, etc.), maximizing the amount of Pt exposed while minimizing the overall amount of the expensive metal, and eliminating the presence of organic capping groups or other contaminants that cover the active surface.

Here, different atmospheric plasma devices including a microplasma and a radio-frequency (RF) plasma torch are shown to be capable of producing Pt and Pt-based alloy nanoparticles without any organic capping molecules and minimal chemical additives. The as-synthesized nanoparticles are characterized by X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) to assess their chemical purity and morphology. We find that when using the microplasma to reduce a Pt precursor in solution, small and non-agglomerated Pt nanoparticles can be directly produced in liquid phase (organic or water based). By controlling the initial amount of the Pt precursor dissolved in solution and the charge injected in the system, the nanoparticle concentration can be tuned [2]. Moreover, this methodology can be applied to bimetallic alloys to reduce the amount of Pt in the electrocatalyst.

In comparison, when using a RF plasma torch, Pt nanoparticles can be produced in the solid phase by plasma reduction of a Pt precursor dispersed on the surface of a carbon support (carbon black, carbon xerogel, carbon nanotubes or graphene) [3]. A mechanism for the plasma reduction of Pt is proposed. It is shown that the size distribution of the particles, their dispersion at the surface, and their quantity in the bulk determined by inductively coupled plasma mass spectrometry (ICP-MS), can be fully controlled by the plasma and preparation parameters.

The Pt nanoparticles synthesized by either method are finally used to fabricate the cathode of a proton exchange membrane fuel cell (PEMFC) using a gas diffusion layer as a substrate. The cell performance, represented by the ratio of the electrochemically active surface area (ECSA) and the catalytic activity, which are comparable to commercial cells, will be discussed in detail.

[1] H.A. Gasteiger et al. *In*: W. Vielstich, A. Lamm and H.A. Gasteiger (eds.), Handbook of Fuel Cells – Fundamentals, Technology and Applications, Wiley, Chichester (UK), **2003**, Vol.3, p. 593.

[2] C. De Vos et al. *J. Phys. D: Appl. Phys.* (**2017**), 50, 105206.

[3] D. Merche et al. *Plasma Process. Polym.* (**2016**), 13, 91–104.

12:00pm **PS+NS+SS-WeM13 Microplasma Spray Deposition of Metal Oxide Nanostructures for Energy Applications**, ***Katherine Mackie***, *M.J. Gordon*, University of California at Santa Barbara

A general, substrate-independent method for plasma deposition of nanostructured, crystalline metal oxides is presented. The technique uses a flow-through, micro-hollow cathode plasma discharge (supersonic microplasma jet) with remote anode to deliver a highly-directed flux of growth species to the substrate. A diverse range of nanostructured materials (e.g., CuO, α-Fe_2O_3, and NiO) can be deposited on any room temperature surface, e.g., conductors, insulators, plastics, fibers, and patterned surfaces, in a conformal fashion. The effects of deposition conditions, substrate type, and patterning on film morphology, nanostructure, and surface coverage will be highlighted. Energy storage application examples to be discussed include NiO on carbon for supercapacitors and CuO for conversion-type Li-ion batteries. The synthesis approach presented herein provides a general and tunable method to deposit a variety of functional and hierarchical metal oxide materials on many different surfaces.

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* **Coburn & Winters Student Award Finalist**

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