Plasma Science and Technology
Room: 24 - Session PS+BI-MoA

Applications of (Multiphase) Atmospheric Plasmas (including Medicine and Biological Applications)
Moderator: G.Y. Yeom, Sungkyunkwan University, Korea

2:00pm **PS+BI-MoA1 Plasmas in Saline Solution Sustained Using Bipolar Pulsed Power Source – Tailoring the Discharge Behavior Using the Negative Pulses**, *H.W. Chang*, C.C. Hsu*, National Taiwan University, Taiwan, Republic of China
Plasmas in saline solutions have been extensively studied due to their wide applications. In this work, plasmas ignited in saline solution were studied. The plasma system consisted of two electrodes immersed in 0.2 M NaCl saline solution. The electrode where the plasma was ignited was a 0.5 mm - diameter Pt wire covered by a glass tube to precisely define the area exposes to the solution. The grounding electrode was a bare platinum wire with the same diameter. Diagnostic tools used included voltage and current probes, an optical emission spectrometer, and a photomultiplier tube. We studied plasmas driven by a bipolar pulse power source using repetitive positive and negative voltage pulses with adjustable width and amplitude. We used the positive voltage pulses to ignite the plasma while using the negative voltage pulses to tailor the electrolytic gas formation amount. Conditions with the positive voltage pulse fixed at +600 V with an 80 μs duration, and the negative pulse varying from 0 to 80 V with the duration ranging from 0 to 20 ms were tested. By changing the duration of each voltage pulses, the bubble dynamics and the plasma behavior can be effectively controlled. By increasing the negative voltage pulse amplitude, we observed a decrease in the maximum currents before the ignition of the plasma from 1.75 to 1.0 A . The time required for plasma ignition upon the onset of the positive voltage pulse was reduced. The above observations can be well explained by the coverage of the electrode surface by electrolytic gas. Optical emission spectroscopy showed that $I_H(656$ nm$)/I_{Na}(588$ nm$)$ ratio increases from zero to 0.0035 when the negative voltage pulse amplitude increases from 0 to 80 V. This clearly showed hydrogen, the electrolytic gas, content in the bubble increased with the increase in negative voltage pulse amplitude. This work was supported by National Science Council of Taiwan, the Republic of China (100-2628-E-002-012 and 101-3113-E-002-002).

2:20pm **PS+BI-MoA2 Low Temperature Plasma Deactivation of Endotoxic Biomolecules: The Effects on Lipid A**, *T.-Y. Chung, J.-W. Chu, D.B. Graves,* University of California Berkeley*, E. Bartis, J. Seog, G.S. Oehrlein*, University of Maryland
Effective removal of infectious organisms and/or biomolecules from medical instruments is essential to prevent infections and disease transmission. Intricate modern instruments are difficult to clean via thermal sterilization since they are often heat sensitive. Furthermore, bacterial endotoxin and prion proteins are known to be particularly resistant to conventional sterilization procedures.[1, 2] Low-temperature plasma is a promising option for surface sterilization of bacteria and deactivation of harmful biomolecules, but mechanisms of endotoxic biomolecule deactivation are poorly understood.[3] Using a vacuum beam system, we study the effects of vacuum ultraviolet (VUV) radiation, oxygen and deuterium radicals on lipid A, the immune-stimulating region of lipopolysaccharide (LPS). The endotoxic activity of lipid A samples is monitored by measuring the secreted interleukin-1β (IL-1β) in human whole blood. The results obtained from *ex situ* transmission Fourier transform infrared (FTIR) spectroscopy, *in situ* quartz crystal microbalance (QCM), *in situ* residual gas analysis and *ex situ* electrospray ionization mass spectrometry (ESI-MS) show that VUV photons cause bulk modification to the penetration depth of photons, ~200 nm. On the other hand, radicals mainly cause chemical etching and modification near the surface of lipid A films. Although the radical-induced etch yield of lipid A is much lower than VUV-induced photolysis, secondary ion mass spectrometry (SIMS) and human whole blood-based assay demonstrate that O and D radicals alter the film surface, leading to significant reduction of film endotoxicity. Important structures governing the endotoxic activity of lipid A, e.g. the fatty acid chains and the phosphate groups, are greatly reduced after radical exposure. Qualitatively similar results are observed when LPS films are exposed to either H atoms or VUV photons in low-pressure plasma. The deactivation

effects of low energy ions and atmospheric pressure air plasma on lipid A films will also be presented.

[1] K. L. Williams, ed., Endotoxins: Pyrogens, LAL Testing and Depyrogenation, Informa Healthcare USA, Inc., New York, 2007.
[2] W. A. Rutala and D. J. Weber, Infect. Control Hosp. Epidemiol. **31**, 107 (2010)
[3] A. von Keudell et al., Plasma Process. Polym. **7**, 327 (2010)

2:40pm **PS+BI-MoA3 Nonthermal Bioplasma Sources and its Interactions to the Microbial, Fungal, Yeast and Living Cells**, *E.H. Choi, Y. Kim, G.S. Cho, G. Kwon, B.K. Min, H. Uhm,* Kwangwoon University, Republic of Korea*, P. Suanpoot,* Maejo University Phrae Campus, Thailand*, G. Lee, R. Jung, B. Park*, Kwangwoon University, Republic of Korea **INVITED**
We have investigated the atmospheric pressure (AP) nonthermal bioplasma sources and their characteristics as well as their interactions with biological cells of microbial, fungal, yeast, and living cells. The electron temperature and plasma density are measured to be about 1.1 eV~ 1.5 eV and $(1~3)\times10^{12}$ cm^{-3} , respectively,for the direct plasma jet and dielectric barrier discharge (DBD) plasma under Ar gas flow. The densities for the reactive oxygen species (ROS) such as the hydroxyl radicals (OH), superoxide anions(O2*⁻), and nitric oxide (NO) have also been investigated in these AP direct plasma, respectively, inside the saline culture media by the ultraviolet optical absorption spectroscopy. Herein, we have investigated the basic interactions of these AP nonthermal bioplasma with the living organisms in morphological and biomolecular aspects. We found that the secondary electron emision coefficient of the biological surface has been drastically increased by atmospheric bioplasma, which indicates the biological surface to be oxidized especially by the hydroxyl (OH) radical species. In order to elucidate the basic mechanisms for the cell shrinking and apoptosis leading to a cell death by the nonthermal bioplasma, the cell membrane potential changes have been measured and investigated inside the culture media based on the ROS density as well as cell capacitances. It is also found that the molecular electron energy band structure in these biological cells have been modified and shifted toward the vacuum surface energy level by the AP nonthermal bioplasmas due to cell oxidation, mainly caused by OH radicals. We have also investigated the confocal Raman spectroscopy and circular dichroism as well as various biological assays to clarify these characteristics.

3:40pm **PS+BI-MoA6 Deactivation of Lipopolysaccharide and Lipid A by Radicals Produced in Inductively Coupled Plasmas**, *E. Bartis*, University of Maryland*, T.-Y. Chung, J.-W. Chu, D.B. Graves,* University of California Berkeley*, J. Seog, G.S. Oehrlein*, University of Maryland
Low temperature plasma (LTP) treatment of surfaces has been shown to degrade and sterilize bacteria as well as deactivate harmful biomolecules [1]. However, a major knowledge gap exists regarding which plasma species e.g. ions, VUV photons, and reactive radicals, are responsible for the modifications required for deactivation. Lipopolysaccharide (LPS) and lipid A, the toxic element of LPS, are the main components of the outer membrane of Gram-negative bacteria and are notoriously difficult to remove from surfaces by traditional sterilization methods [2]. In this study, LPS- and lipid A-coated silicon substrates were exposed to low pressure plasma-generated Ar and H radicals isolated from an inductively coupled LTP source by employing a gap structure [3] to examine the effects of plasma composition on etch rates and chemical properties. Bioactivity of LPS was measured using an enzyme-linked immunosorbent assay (ELISA). Ar neutrals caused a 5% reduction in bioactivity whereas exposure to H radicals using the same plasma operating conditions caused a 25% reduction in bioactivity. Ellipsometric data shows that H radical-only exposures cause less than 2 nm of material removal, indicating that surface modification is the major cause of deactivation and that complete etching and removal is not necessary. These modifications can inhibit the binding of receptor molecules, whose binding depends on a variety of interactions such as hydrophobic and electrostatic interactions and lock-and-key mechanisms. After plasma processing, samples were characterized by vacuum transfer to x-ray photoelectron spectroscopy (XPS) to study the chemical changes occurring on the film surface. With XPS, we observed that plasma-generated H radicals produce a C-rich surface by effectively removing O, N, and P, the latter of which is from phosphate groups that contribute to the pyrogenicity. The C 1s spectra shows a clear loss of N-C=O and O-C=O groups. This loss leads to the removal of lipid A's aliphatic chains, which are responsible for its toxicity. Direct H2plasma treatments also remove O, but fast material removal causes an increase in N and P due to the exposed core and O-chain on LPS. Radical-only ELISA results will be compared to direct and VUV-only treatments where material removal is significantly

---

* Coburn & Winters Student Award Finalist

greater. This result is especially true for direct Ar plasmas, where modification/etching is dominated by ion bombardment. Our results compare favorably with complementary VUV/radical beam studies of lipid A.

[1] A. von Keudell et al., Plasma Process. Polym. **7**, 327 (2010)

[2] E. T. Rietschel et al., FASEB J. **8**, 217 (1994)

[3] L. Zheng et al., J. Vac. Sci. Technol. A **23**, 634 (2010)

4:00pm PS+BI-MoA7 Localised, Non-Contact Surface Modification with Microplasma for Biotechnological Applications, *S.A. Al-Bataineh, E.J. Szili, D.A. Steele, N.H. Voelcker, H.J. Griesser, R.D. Short*, University of South Australia

Localised surface modification of "open" surfaces is important for many biotechnological applications. In this study, we describe the utilisation of microcavity plasma arrays for localised surface modification of materials in a non-contact approach. In contrast to the current methods for localised surface modification, our method achieves spatially controlled surface modification without the use of a physical mask, photolithography or contacting the surface. Therefore, it provides the opportunity to reduce the number of modification steps and thus the cost of surface engineering processes. To this end, a 7 x 7 microcavity plasma array device (each cavity is separated by 500 µm and has a diameter of 250 µm with a depth of 55 nm) was manufactured and operated in helium at atmospheric pressure to generate, under optimised operating parameters, spatially separated modified regions on passivated surface coatings. The microplasma-patterned coatings were then used to control the spatial distribution of biomolecules such as proteins by allowing protein adsorption onto the modified regions whereas the rest of the coating remains non-fouling. Therefore, this approach resulted in spatially separated areas of immobilised protein. These surfaces were also used to control the spatial distribution of other biomolecules as well as living cells.

4:20pm PS+BI-MoA8 Biocompatible Nanocomposites Synthesized by Gas-Liquid Phases Plasmas, *T. Kaneko, Q. Chen, R. Hatakeyama*, Tohoku University, Japan **INVITED**

Recently, multiphase plasmas, particularly gas-liquid phases plasmas have attracted much attention as fundamental and application researches [1], because the non-equilibrium plasmas in gas phase can produce the various kinds of chemically active ions and radicals which react with nano- and bio-materials stably existing in liquid. As one of the promising applications of the gas-liquid interfacial discharge plasmas (GLIDPs), the synthesis of various kinds of nanoparticles [2] is advantageous in that toxic reducing agents are unnecessary and the synthesis is continuous during the plasma irradiation. In addition, the GLIDPs are also used in the biomedical field, for example, the synthesis of gold nanoparticles (AuNPs) conjugated with biomolecules such as DNA. The DNA conjugated AuNPs (DNA-AuNPs) work as vectors to deliver DNA into living cells because the AuNPs can be efficiently manipulated by a light field. Furthermore, the DNA-AuNPs are attempted to be encapsulated into carbon nanotubes (CNTs) to protect the DNA from the ambient environment.

The GLIDP is generated between the bottom liquid and top metal electrodes in Ar gas (20 kPa) by applying a pulse voltage (20 kHz) to the liquid electrode. The liquid electrode consists of aqueous chloroauric acid trihydrate (HAuCl$_4$•3H$_2$O) (0.1 mg/ml) with DNA. A single-stranded DNA is used as the conjugated material, which consists of 30 bases of cytosine or guanine. In the synthesis of the DNA-AuNP encapsulated CNTs, double-walled carbon nanotubes (DWNTs) are adopted to be used because of their large inner diameter.

Depending on the DNA concentration, the resultant water-soluble AuNPs take on pink and purple. The different colors originate from the particle size and interparticle distance which determine the absorption wavelength of the surface plasmon resonance of the AuNPs. Interestingly, these phenomena depend on the types of DNA base, which are attributed to the difference in the binding energy of the DNA base. Therefore, we can control the size and assembly of the AuNPs by changing the DNA type and concentration [3].

In order to encapsulate the negatively charged DNA-AuNPs into the DWNTs, a positive DC voltage is applied to the DWNTs put on the substrate immersed in the GLIDP. The transmission electron microscope images of the resultant products show that the number of the DNA-AuNPs encapsulated into DWNTs increases with an increase in the positive DC voltage.

[1] T. Kaneko, K. Baba and R. Hatakeyama: J. Appl. Phys. **105**, 103306 (2009).

[2] T. Kaneko, Q. Chen, T. Harada and R. Hatakeyama: Plasma Sources Sci. Technol. **20**, 034014 (2011).

[3] Q. Chen, T. Kaneko, and R. Hatakeyama: Chem. Phys. Lett. **521**, 113 (2012).

5:00pm PS+BI-MoA10 Organization of Dielectric Barrier Discharges in the Presence of Structurally-Inhomogeneous Wood Substrates, *O. Levasseur,* Université de Montréal, Canada, *A. Bouarouri, N. Naudé, R. Clergereaux, N. Gherardi,* Université de Toulouse, UPS, INPT, LAPLACE, France, *L. Stafford*, Université de Montréal, Canada

There has been a growing interest in the use of dielectric barrier discharges (DBDs) for many applications, especially for the treatment of heat-sensitive materials such as polymers. Some studies have also reported a self-organization of these discharges which can manifest itself in two ways : i) the auto-organization of filaments or micro discharges in a filamentary DBD or ii) the formation of regular spatio-temporal patterns in a glow-like discharge. Several types of patterns such as hexagonal arrays or concentric rings have been observed for various gases and system configurations. We have recently extended the range of applications of DBDs to the functionalization of wood surfaces with the objective of improving its durability following natural weathering. However, the application of DBDs to the modification of wood presents additional complications compared to traditional substrates due not only to the highly porous nature of wood which can produce significant outgassing but also to the presence of "early" vs. "late wood" sections which can introduce local modification of the properties of the dielectric exposed to plasma. In this work, we examine the organization of DBD in the presence of complex wood substrates using optical imaging and current-voltage (I-V) characteristics. For Douglas pine samples, the structural inhomogeneities of the wood substrate was found to produce non-uniform light emission patterns while maintaining homogeneous-like I-V characteristics. Experiments performed on samples with various fractions of "early" vs. "late" wood sections showed that the plasma emission was always more intense on the "early" wood. The charge flow pattern was also analyzed using surface potential measurements. Both sections exhibited decaying behaviors, with time constants, t, of 40 s for late wood and 10 s for early wood. Based on these results and the predictions of a simple electrical model of the discharge, the organization was ascribed to a spatial modulation of the relative dielectric permittivity on "early" versus "late" wood affecting the local voltage applied to the gas, and thus the local discharge current which is directly related to the plasma emission.

5:20pm PS+BI-MoA11 Role of Substrate Outgassing on the Formation Dynamics of Either Hydrophilic of Hydrophobic Wood Surfaces in Atmospheric-Pressure, Organosilicon Plasmas, *O. Levasseur, L. Stafford,* Université de Montreal, Canada, *N. Gherardi, N. Naudé,* Université de Toulouse, UPS, INPT, LAPLACE, France, *P. Blanchet,* FPInnovations, Canada, *B. Riedl,* Université Laval, Canada, *A. Sarkissan*, Plasmionique, Canada

Dielectric barrier discharges (DBDs) were thoroughly investigated over the last several years with one of the main goals being the achievement of a homogeneous discharge at high operating pressure in various gas mixtures. This keen interest is mainly driven by the fact that atmospheric-pressure DBDs present major advantages over low-pressure plasmas for polymer treatments, one of the most important being the ability to work with cold plasmas without the use of high-end vacuum pumping systems. Over the last decade many precursors, such as organosilicon compounds like hexamethyldisilazane (HMDSN) and hexamethyldisiloxane (HMDSO), were added to these cold, atmospheric-pressure plasmas for PECVD applications and a wide variety of coatings have been obtained by such methods. Application of DBDs to the treatment of polymers is however much more challenging than for conventional substrates such as Si or SiO2. This can be not only be attributed to the highly complex chemical nature of most polymers but also to their generally porous microstructure which can release impurities in the discharge either from plasma-substrate chemical reactions or from sample outgassing (if not pumped-down beforehand). Such impurities can greatly alter the discharge stability and gas-phase kinetics which are both known to play an important role on the plasma deposition dynamics. In this work, we capitalize on the very porous nature of wood to examine the influence of substrate outgassing during PECVD on the stability of a N$_2$-HMDSO discharge and on the evolution of the properties of plasma-deposited thin films over sugar maple and black spruce wood samples. Current-voltage characteristics revealed a transition from a filamentary to a homogeneous discharge with increasing plasma treatment time, *t*. Based on optical emission spectroscopy, the filamentary behavior was ascribed to the release of air and humidity from the wood substrate following plasma exposure which produced significant quenching of N$_2$ metastables. This effect vanished at longer treatments times due to the nearly complete "pumping" of products from the substrate and the progressive deposition of a "barrier" layer. Analysis of the surface wettability through static, water contact angles (WCAs) and of the surface composition through FTIR and XPS indicated that for *t* < 10 min, the wood surface was more hydrophilic due to the formation of a SiO$_x$ layer, a typical

behavior for HMDSO deposition in presence of oxygen. On the other hand, for $t > 10$ min, the static WCA increased from ~50° up to ~140° due to the deposition of hydrophobic $Si(CH_3)_3$-O-$Si(CH_3)_2$ and $Si(CH_3)_{3,2}$ functional groups.

Authors Index

Bold page numbers indicate the presenter