Plasma Science and Technology Division
Room B131 - Session PS1-MoA

Plasma-Liquid Interactions, Medicine, and Agriculture

Moderators: Kazunori Koga, Kyushu University, Japan, Deborah O'Connell, University of York, UK

1:40pm **PS1-MoA-1 Peroxynitric acid ($HOONO_2$) Chemistry in Plasma-treated Water for Effective and Safety Disinfection*, Katsuhisa Kitano,*** Osaka University, Japan*; S Ikawa, Y Nakashima,* Osaka Research Institute of Industrial Science and Technology, Japan*; T Yokoyama,* Osaka University, Japan*; A Tani,* Kobe University, Japan **INVITED**

Plasma medicine is one of attractive research areas in the area of plasma application. By the exposure of low temperature atmospheric plasma to living organism (human body, bacteria, and so on), positive effect is expected. As biological environment is wet condition, plasma induced chemical reactions in liquid should be considered.

For the plasma disinfection of human body, we have developed the reduced-pH method with direct plasma exposure, which brings stronger bactericidal activity in the liquid at lower pH condition, where the threshold is pH 4.8. The enhancement is thought to be due to hydroperoxy radical (HOO•) generated from superoxide anion radical (O_2^-•) by acid dissociation equilibrium (pKa 4.8). Electrically neutral HOO• could easily penetrate into cell to bring intracellular oxidative stress. In addition, we found that the plasma-treated water (PTW) also has strong bactericidal activity under acidic condition in the same manner. Physicochemical properties of PTW are discussed based on chemical kinetics. Lower temperature brings longer half-life, and the bactericidal activity of PTW can be kept by cryo-preservation. This means that PTW with higher bactericidal activity could be obtained by longer plasma treatment under enough low temperature. High performance PTW, corresponding to the disinfection activity of 22 log reduction (against Bacillus subtilis spore), can be obtained by special plasma system equipped with cooling device. The bactericidal activity of our PTW is much stronger than others.

Many researchers are interested in this area of PTW, where the waters are treated / activated by their original devices. For scientific understanding, we should discuss based on chemical species. Although PTW has many chemical components, respective chemical components in PTW were isolated by ion chromatography. Active ingredient of PTW was successfully purified to be confirmed to $HOONO_2$ (PNA: peroxynitric acid). Although the existence of PNA has been known since 100 years ago, sterilization by PNA has never been reported in past papers. PNA is known to release HOO• by radical cleavage. So we conclude that PNA is a key chemical species of cryo-preserved PTW with the reduced-pH method.

From the experimental results of chemical synthesis, PNA is effectively generated from HNO_2 and H_2O_2 under extremely acid condition (pH < 2). Although averaged pH of PTW is about 3~4, pH at the surface of PTW (limited area of interface between plasma and liquid) during plasma treatment is thought to be enough low that PNA can be synthesized from HNO_2 and H_2O_2 supplied from plasma. In the presentation, peroxynitric acid chemistry in PTW will be discussed in detail.

2:20pm **PS1-MoA-3 Impact of Solution Properties on Plasma Formation in DC Plasma Electrolysis*, Hernan E. Delgado*[1]**, *D Bartels, P Rumbach, D Go,* University of Notre Dame

A common configuration used in plasma-liquid interactions is that in which a direct current (DC) gas discharge is generated between a liquid and a metal. Under this configuration, known as plasma electrolysis or glow-discharge electrolysis, the liquid itself functions as a plasma cathode or anode, for a positive or negative DC bias, respectively. However, it is not clear exactly how the liquid participates in the formation and sustaining of the plasma, including charge transfer at the plasma-liquid interface. This is especially true when the liquid is acting as a cathode, and secondary emission from the liquid is ostensibly required to sustain the plasma. In this work, we use measurements of the breakdown and discharge voltages to understand this process. Voltage measurements for an argon plasma in contact with an aqueous solution are conducted in an electrochemical H-cell reactor to test for conditions that would facilitate secondary emission from the liquid. Voltage measurements across the plasma show a strong dependence on ionic strength, and no dependence on pH (from pH = 0 to 14) while controlling for ionic strength. The voltage was also found to be strongly dependent on the temperature of the liquid. Free radical scavengers nitrite and nitrate had no significant effect on the plasma voltage even at 1.0 M concentration, suggesting that the solvated electron, the pre-solvated electron, and the hydrogen atom do not play a crucial role in secondary emission as previously proposed.

2:40pm **PS1-MoA-4 Plasma Reactive Species Formation in Liquids*, Sylwia Ptasinska,*** University of Notre Dame **INVITED**

Plasma reactive species which are directly originated in an atmospheric pressure plasma jet (APPJ) and/or indirectly produced in liquids can drive a plethora of chemical reactions. Despite the rapid growth in interest in this type of plasma, our fundamental and comprehensive knowledge of the chemistry which plasma induces in multiphase systems is still needed to be achieved. One of the approaches to obtain this goal is a development of sophisticated interrogation techniques to provide such characterization. In our laboratory, we developed in situ optical absorption technique, and used ferrous sulfate (Fricke) solution in which species were detected under plasma interaction to quantify the total yield of these species under different experimental conditions. A yield of ferric (Fe3+) ions measured using this technique was attributed to the formation of plasma reactive species provided and/or originated in the solution. The results indicated that the number of reactive species formed was proportional to plasma frequency and voltage. However, the Fe3+ yield per pulse decreased with increased frequency. To obtain a better understanding of the processes and species involved in the chemical reactions due to plasma exposure, Fe3+ yields were calculated and compared to the experimental data. At higher frequencies, there was insufficient time to complete all reactions before the next pulse reached the solution; at lower frequencies, the Fe3+ yield was higher because of the relatively longer time available for reactions to occur. It is also known that gas composition of APPJ as well as ambient conditions influence plasma chemistry and thus also reactions in liquids which are in contact with plasma. We performed systematic studies to probed changes in plasma electrical properties, by adjusting the fraction of oxygen and water vapor in the plasma jet environment and feed gas. While DNA was used to identify chemical changes that occurred in the plasma jet under these various experimental conditions. We determined optimal conditions at which increase in the damage to the molecular probe was significant. This increase can be attributed primarily to the formation of reactive species caused by water and oxygen decomposition in the APPJ. At the same time, we observed no change in the plasma electrical power when oxygen or water vapor were added to the jet environment but decreased when these gases were introduced to the feed gas. This indicates that the effects of plasma chemistry supersede those due to the power applied for APPJ ignition.

3:20pm **PS1-MoA-6 In-flight Synthesis and Online Characterization of Silver Nanoparticles from Aerosol Droplets Reacting in a Non-thermal Plasma*, Tommaso Gallingani,*** Alma Mater Studiorum-University of Bologna, Italy, Italia*; N Abuyazid,* Case Western Reserve University*; M Gherardi, V Colombo,* Alma Mater Studiorum-University of Bologna, Italy*; C Hogan,* University of Minnesota, Minneapolis*; M Sankaran,* Case Western Reserve University

Because of their unique features and low-temperature chemistry, non-thermal, atmospheric-pressure (AP) plasmas have attracted interest for material synthesis in multiphase environments where the plasma is in contact with a liquid surface. In the most common configuration, the reaction interface is highly localized, leading to inhomogeneities and mass transport limitations. In light of these issues, liquid water jet and a liquid aerosol have been proposed as alternative strategies that allow continuous liquid flow and promote more controlled reaction. However, applications of these multiphase systems are complicated and limited by lack of knowledge of reaction mechanisms.

Here, we carried out a detailed study of a flow-through, liquid-droplet plasma system using an online ion mobility spectrometry (IMS) system to characterize precursor to particle conversion. IMS measures the electrical mobility of aerosol particles providing real time size distribution. The focus of our study was silver nitrate ($AgNO_3$) which has been well-studied in plasma-liquid synthesis and, thus, provides a straightforward chemistry to benchmark our results . Liquid droplets containing $AgNO\text{-}_3$ were produced by a Venturi effect nebulizer and carried in by an argon flow into an AP dielectric barrier discharge (DBD). The DBD configuration was a quartz tube with two ring electrodes in parallel to avoid any metal in contact with the plasma and driven by an alternating current high voltage generator. The effluent of the reactor was diluted by a flow of nitrogen gas and coupled to the inlet of a commercial IMS system. For a given flow rate, precursor

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[1] **Coburn & Winters Student Award Finalist**

concentration, and plasma power, our results show that the mean particle diameter decreases from 38 to 26 nm when the plasma is on which could be ascribed to $AgNO_3$ reduction to silver (Ag). The synthesized Ag nanoparticles (NPs) were collected either by electrostatic precipitation or filtration for materials analysis. NPs size distribution and morphology were assessed by transmission electron microscopy and found to have good agreement with IMS data. Ultraviolet-visible absorbance showed the well-known localized surface plasmon resonance peak for Ag at approximately 400 nm, confirming a successful conversion. We also performed a control experiment with a diffusion dryer to remove the water and only introducing dried $AgNO_3$. The lack of any reduction to Ag NPs suggested that the mechanism involves water and plasma species alone cannot reduce $AgNO_3$. This study provides important insight into liquid-droplet-based multiphase plasma reactors which are a novel approach to synthesizing NPs from precursors that are not available as a vapor.

4:00pm **PS1-MoA-8 Plasma-assisted Fabrication and Functionalization of Materials for Applications at the Nano-biointerface***, Cristina Satriano,* University of Catania, Italy **INVITED**

Surface tailored (nano)materials are of striking interest to better control protein/material and cell/material interactions at the sub-molecular level.

Current fabrication of nanomaterials is facing the following two challenges: high selectivity toward specific chemical compositions or morphologies and their scalable production. This usually requires new synthesis/functionalisation conditions beyond the conventional approaches.

Plasma chemistry presents an opportunity to explore these features and to potentially trigger new surface-driven biological effects. Indeed, the unique synergy of physical and chemical phenomena that occur in the low temperature plasmas has led to an ever-increasing effort to find solutions to currently problematic medical, agricultural, cosmetic and environmental problems by using multifaceted cold plasma environment.

In this paper, the latest progress in the plasma-assisted fabrication and/or functionalization of materials from nanoparticles to low-dimensional nanostructures, including graphene oxide, are briefly reviewed, with a special focus on discussing plasma properties responsible for the nanomaterial growth with high throughput, desired compositions and shapes, or narrow size distributions as well as for the surface functionalization with some control on the ageing processes.

Case studies on plasma-synthesized plasmonic nanogold and nanosilver with tunable optical and electrical properties and plasma surface-modified polymers and nanocarbons at the interface with peptides/proteins, extracellular matrix, supported lipid bilayers and cells are discussed. An outlook of challenges and opportunities for further advancement in this emerging field is given.

4:40pm **PS1-MoA-10 Cold Plasma Jets, Liquids and Biomaterials for Bone Cancer Therapy***, Cristina Canal,* Universitat Politècnica de Catalunya, Spain **INVITED**

Over the last few years, significant attention has been paid to biomedical applications of Atmospheric Pressure Plasmas (APP), and especially to the involvement of reactive species (RONS) in selective cancer cell death [1] without damaging surrounding healthy tissues [2]. The anti-cancer properties of the APP have been described in many cancer cell lines, such as breast, skin, lung, pancreas, brain cancers among others and only more recently in bone cancer cells [3-4]. The biological effects of plasmas have been observed also in a wide variety of plasma activated liquids (PAM) [5], opening the door for minimally invasive therapies.

Despite being rare, Osteosarcoma (OS) is the most common primary bone tumorbeing the most common solid tumor in teenagers and the third most common malignancy in children. Our research focuses on the effects of plasmas on osteosarcoma.

We have investigated the effects of different plasma jets in the generation of RONS in liquids of biological interest. OS cells show higher sensitivity to PAM treatment than healthy cells, activating apoptosis, DNA damage and deregulating cellular pathways mediated by c-JUN, AKT, AMPK or STAT3 [6].

However, injection of a liquid in the body associates it being washed away by the blood flow, so development of efficient vehicles which allow location and delivery of RONS to the diseased site is lacking. Therefore, it is our interest to elucidate the potential of hydrogels to generate and store RONS generated by plasmas. Hydrogels are highly hydrated networks of cross-linked polymer chains whose features such as biocompatibility make them great candidates for the design of advanced biomaterials. We will discuss different hydrogels; in general, their physic-chemical properties remain unchanged by the plasma treatment, while the hydrogels show several-fold larger capacity for generation of RONS than a typical PAM – the absolute amounts generated depending a lot on the chemistry of the hydrogel. The hydrogels show different capacity for release of RONS depending on their properties. The plasma-treated hydrogels show efficient killing of OS cells, related to the different RONS generated.

Acknowledgement. This project has received funding from ERC under the European Union’s Horizon 2020 research and innovation programme (grant agreement No714793).

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2. M. Keidar et al, Physics of Plasmas, 20, 57101 (2013)

3. C. Canal et al, Free Radical Biology and Medicine, 110, 72 (2017)

4. D. Gümbel et al, Anticancer Research, 36, 5915-5922 (2016)

5. A. Khlyustova et al, Frontiers Chem. Sci. Eng. (2019)

6. J. Tornin et al, Scientific Reports (Under revision 2019)

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