SIMS Solutions in Materials and Life Sciences
Room Great Lakes C - Session SS-ThM2

Environmental

Moderators: Felicia Green, Rosalind Franklin Institute, **Zihua Zhu**, Pacific Northwest National Laboratory

8:40am **SS-ThM2-1 Liquid ToF-SIMS Revealing the Oil, Water, and Surfactant Interfacial Evolution***, **Xiao-Ying Yu**,* Oak Ridge National Laboratory*; Y. Shen,* Ocean University of China*; J. Son, Z. Zhu,* Pacific Northwest National Laboratory

Bilgewater formed from the shipboard is regarded as a major pollutant in the marine environment. Bilgewater exists in a stable oil-in-water (O/W) emulsion form. However, little is known about the O/W liquid-liquid (l-l) interface. Traditional bulk characterization approach is not capable of capturing the chemical changes at the O/W l-l interface. Although surfactants are deemed essential in droplet formation, their roles in bilgewater stabilization are not fully revealed. We have employed novel in situ chemical imaging tools including in situ scanning electron microscopy (SEM) and in situ time-of-flight secondary ion mass spectrometry (ToF-SIMS) to study the evolving O/W interface using a NAVY bilge model for the first time. The droplet size distribution (DSD) does not change significantly without the addition of X-100 surfactants at static or rocking conditions. Both the oil components and the water clusters are shown to evolve over time at the O/W droplet interface by in situ liquid SIMS imaging. Of particular interest to droplet stabilization, the contribution of surfactants to the aged bilge droplets becomes more significant as the droplet size increases. The higher mass surfactant component does not appear on the droplet surface immediately while many lower mass surfactants are solvated inside the droplet. We have provided the first three-dimensional images of the evolving O/W interface and demonstrated that in situ surface chemical mapping is powerful to reveal the complex and dynamic l-l interface in the liquid state. Our observational insights suggest surfactants are important in mediating droplet growth and facilitating effective separation of bilgewater emulsion.

9:00am **SS-ThM2-3 Investigation of Bacteria/Model Hybrid Core-Shell Nanoparticles Interactions by an Innovative Combination of Surface Analysis and Mass Spectrometry Techni***, S. Fernández-Castillo Suárez , **Cecile Courreges**, J. Jiménez Lamana, S. Godin, S. Nolivos, R. Grimaud, J. Szpunar, J. Allouche,* Université de Pau et des Pays de l'Adour, E2S UPPA, CNRS, IPREM, France

The increasing use of nanomaterials in our lifestyles induce significant problems of pollution in the environment, particularly with respect to microbes and bacteria, which are ubiquitous in ecosystems. However, the mechanisms of interaction between bacteria and nanoparticles are still poorly studied. In particular, the physico-chemical parameters governing the complex processes of degradation of nanoparticulate organic matter and/or the mechanisms of recognition of substrate nanoparticles by bacteria are still unknown[2]. In this project, the study of these parameters is carried out through a multidisciplinary strategy involving a combination of several domains including nanoscience, analytical chemistry and microbiology. In this context, model core-shell hybrid nanoparticles based on hierarchical structure involving gold@silica@gelatin morphologies were designed. Gelatin was used as organic substrate for *Alteromonas macleodii*, the marine bacteria species selected for this study. The characterization of nanomaterials and the monitoring of enzymatic degradation processes and bacteria/nanoparticle interactions (Fig. 1), were achieved through an innovative combination of surface analysis and mass spectrometry techniques,[3,4] including Time-of-flight secondary ion mass spectrometry (ToF-SIMS Tandem MS), X-ray photoelectron spectroscopy (XPS), Auger microscopy (AES), liquid chromatography electrospray ionization mass spectrometry (LC-ESI-MS) and Single particle inductively coupled plasma mass spectrometry (SP-ICP-MS). On one hand, SP-ICP-MS and AES analyses allow the quantification of nanoparticle binding mechanisms on cells by following the gold core particles used as markers. On the other hand, ToF-SIMS Tandem MS, XPS and LC-ESI-MS techniques enable to identify peptide fragments originating from the degradation of gelatin on the surface of model nanoparticles. The results obtained and the strategy implemented thus open the way to the determination of key parameters governing the interactions between nanoparticles and bacteria, which are of primary importance in environmental degradation processes but also in the fight against pathogens.

References: [1] F. Ameen, K. Alsamhary, J.A. Alabdullatif, S. AlNadhari, Ecotoxicol. Environ. Saf. 213 (2021), 112027. [2] M. Mansor, J. Xu, Environ. Microbiol. 22(9), (2020), 3633–3649. [3] C. Courreges, M. Bonnecaze, D. Flahaut, S. Nolivos, R. Grimaud, J. Allouche, Chem. Commun. 57 (2021), 5446-5449. [4] L. Yin, Z. Zhang, Y. Liu, Y. Gao, J. Gu, Analyst 144, (2019), 824–845.

9:20am **SS-ThM2-5 Surface and Functional Characterization of Nanostructured Thin Films for Environmental Remediation***, **Enrica Maria Malannata**, A. Auditore, A. Licciardello,* Università di Catania, Italy

Nowadays the presence of pollutants in water represents an ever greater and difficult problem to solve. Efficient removal of contaminants from aqueous solutions requires advanced oxidation processes (AOPs). This can be accomplished by different methods, such as electrocatalysis, photocatalysis and photo-electrocatalysis, involving the use of materials that allow the fast removal of the pollutant with high degradation efficiency. The photo-electrocatalytic approach appears to be among the most promising processes because it combines the advantages of photocatalysis and electrocatalysis [1].

The most used material in this regard is TiO_2 which, however, shows several problems including a band gap around to 3.0-3.2 eV that does not allow the absorption of visible light.

With appropriate surface modifications such as the presence of phosphate anions, it is possible to improve the generated photocurrent [2] to obtain a best performing material in photo–electrocatalysis applications.

In this work the surface of nanostructured TiO_2-based films were chemically modified to improve its electro-, photo-electro and photocatalytic performance. In particular, mesoporous TiO_2 films were engineered using the zirconium phosphate (ZP) modification [3] in order to improve the sensitivity to sunlight, the electrical properties, and the thermal stability of the material.

We used extensively TOF-SIMS for obtaining space-resolved information on the functionalization of the mesoporous oxide, necessary for the engineering and monitoring of the material modification protocol. Moreover, TOF-SIMS allowed to monitor the photocatalytic reactions at the mesoporous oxide surface providing information on the degradation pathway under solar light irradiation. In particular the present study considered, as target molecules, both model dyes such as Rhodamine B and real-world persistent pollutants such as pesticides. Understanding the degradation pathways occurring at the photocatalyst surface, indeed, is an important step for the design of specific functionalization processes aimed to the improvement of the performances of the material.

[1] T.H. Jeon et al. ACS Catal. 8 (2018) 11542–11563.

[2] L. Jing et al. Energy Environ. Sci. 5 (2012) 6552–6558.

[3] S. Vitale et al. J. Vac. Sci. Technol. B. 34 (2016) 03H110.

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