Beyond SIMS
Room Great Lakes Promenade & A1 - Session BS-TuP
Beyond SIMS Poster Session

BS-TuP-1 Exploring the Role of Fe-C-Al Sites for the Low Temperature CO Oxidation over Fe-oxide/Al2O3 via ToF-SIMS*, Byeong Jun Cha,* Korea Basic Science Institute, Republic of Korea*; Y. Kim,* Sungkyunkwan University (SKKU), Republic of Korea*; C. Choi, M. Choi,* Korea Basic Science Institute, Republic of Korea

Development of low temperature operating catalysts has been one of the challenges in exhaust gas catalysis since the most commonly used Pt-group catalysts are generally active above 150 °C causing 'cold-start emission'. Fe-oxide nanoparticle catalysts have been studied extensively due to their high low-temperature activity and thermal stability, and many experimental/theoretical studies have been conducted to unveil the relationship between the structure and activity of the Fe-oxide nanocatalysts. In the present work, ToF-SIMS technique, which has not been used widely on iron oxide nanocatalysts, was utilized to elucidate the structure-activity relations on Fe-oxide/Al_2O_3 for the low temperature (~50 °C) CO oxidation. The combined results of various surface analyzing tools including ToF-SIMS showed a scaling relationship of ternary interfacial sites of Fe-C-Al with the CO oxidation activity below 50 °C, indicating that the Fe-C-Al species facilitate low temperature CO oxidation. This work shows that ToF-SIMS can provide valuable information on the structure-activity relations in heterogenous catalysts.

BS-TuP-3 Evaluation of Multi-Depth Modifications of Metal-Oxide Nanotubes*, Swathi Naidu Vakamulla Raghu,* University of Siegen, Germany

Metal-oxide (MO) surfaces have successfully been modified to elicit surface functionality different than the parent material via facile application of self-assembled monolayers (SAM). Previously reported MO surfaces demonstrate superhydrophobicitywhen functionalized with phosphonic acid carbohydrate molecules.[1] In this work, we shed light on the role of SAM facilitated hydrophobic-effect as a result of application technique, i.e., immersion in bulk solution (BI) and micro-contact printing (µCP).These modifiedZrNTs were evaluated along their tube length in the depth-profiling mode using time-of-flight secondary ions mass spectrometry (ToF-SIMS). Using the depth profile mode, we were successfully able to ascertain the presence of targeted molecules at various depths inside the nanotubes. These results were used to provide in proof the possibility to develop multi-depth and multi-functional modifications within nanotubes as shown in Fig. 1a. Herein, the nanotube walls could effectively be functionalized at different depths via wet-chemistry and soft-lithography techniques devoid of clean-room fabrication.[2]In combination, with the developed synthesis and characterization strategies of ZrNT, we are able to demonstrate an enhanced functionality in addition to tailor-made storage capabilities of such nanotubular surfaces. The nanotube reservoirs were evaluated for volumetric storage via simulated dye-release behaviour as seen in Fig. 1b. Such nanotubular reservoirs developed on the implant surface would be capable of facilitating developmental strategies towards controlled multi-drug release models that can even elicit sequential release of drugs to limit clotting, inhibit infection and ultimately promote healing.

REFERENCES

[1]S.N. Vakamulla Raghu, M.S. Killian, Wetting behavior of zirconia nanotubes, RSC Adv. 11 (2021) 29585–29589. https://doi.org/10.1039/D1RA04751E.

[2]S.N.V. Raghu, G. Onyenso, S. Mohajernia, M.S. Killian, Functionalization strategies to facilitate multi-depth, multi-molecule modifications of nanostructured oxides for triggered release applications, Surf. Sci. 719 (2022) 122024. https://doi.org/10.1016/j.susc.2022.122024.

BS-TuP-5 In Situ Liquid Secondary Ion Mass Spectrometry - a Unique Tool for in Situ Molecular Analysis of Various Liquids and Solid-Liquid Interfaces*, Zihua Zhu,* PNNL

Secondary ion mass spectrometry (SIMS) is a powerful surface analysis tool with several unique advantages. It can provide elemental, isotopic and molecular information with excellent sensitivity and decent spatial resolution. SIMS has been extensively used in semiconductor industry and increasingly important in scientific research. However, SIMS is a high-vacuum technique, and it has been normally used for analysis of solid samples. In situ liquid SIMS, which was developed in Pacific Northwest National Laboratory about 11 years ago, can be used for molecular examination of various liquids and liquid interfaces, providing critical information that any other techniques can hardly provide. In the last several years, in situ liquid SIMS has been successfully used to resolve some interesting scientific questions in energy, biology, environment and other fields. In this presentation, the principle of in situ liquid SIMS and its major applications will be summarized.

BS-TuP-7 Surface Modification of Steel, Molybdenum and Tungsten by the Use of Two Techniques: Electron Beam Scanning and Electric Discharge Machining – SIMS and GDMS Maps*, Piotr Konarski,* *J. Ażgin, A. Zawada,* Łukasiewicz Research Network - Tele and Radio Research Institute, Poland*; S. Feng ,* Department of Mechanical Engineering, National Taipei University of Technology. , Taiwan*; C. Chien ,* Chien's Scientific Company, Taiwan*; D. Sheu,* Department of Mechanical Engineering, National Taipei University of Technology, Taiwan

Process of surface modification of steel (s235 and ss304), molybdenum and tungsten samples was carried out with the two techniques - by a high-energy electron beam line scanning in vacuum in a device used for electron beam welding, and by a technique of electric discharge machining (EDM) in which samples are submerged in dielectric fluid.

In the case of electron beam technique we use a beam of 18 keV energy and approx. 500 µm diameter, which is linearly scanned over the surface of the samples at a speed of 0.5 m/s. The used beam currents of 0.5, 1, 2, 5 and 10 mA correspond to the transmitted energy ranging from 10 to 200 J per 10 mm long line scan lasting 0.02 s.

In case of EDM [1] we use electrical energy to generate the spark between the tool made of copper and a workpiece so that material removal is taking place from the sample surface by local melting or vaporization. EDM pulse generator is set for discharge voltage from 80 V to 30 V with calculated charging time = 4.7∗10e-5 s and discharge time = 9.8∗10e-9 s. We use processing time from 100 to 2200 s to erode 10 mm long and 1 mm wide grooves. Deposited energy for such grooves ranges from 10 to 220 J.

For mapping of the modified samples we use two quadrupole-type mass analyser systems: SIMS and glow discharge mass spectrometry (GDMS). Using the two techniques of imaging one can acquire a quantifiable image of the elemental distribution from a sample's surface.

SIMS maps are registered due to scanning of a 100 nA, 5 keV O_2^+ beam over area of 3x3 mm, in the Hiden SIMS Workstation apparatus [2], while GDMS maps are obtained with SMWJ-01 system [3], in which the glow discharge of 0.8 mA current at a voltage of 1.2 kV DC is used. GDMS measurements are carried out by moving the sample line by line in the range of 7x7 mm above the stationary cell of the glow discharge.

This work is supported by the National Center for Research and Development, Poland and Ministry of Science and Technology, Taiwan (Task ID: PL-TW/VII/4/2020).

[1] Sheu, D. Y. (2004) *Journal of Micromechanics and Microengineering*, *15*(1), 185.
[2] Hiden Analytical, 420 Europa Boulevard, Gemini Business Park, Warrington, WA5 7UN, UK
[3] Konarski, P., Miśnik, M., & Zawada, A. (2016) *Journal of Analytical Atomic Spectrometry*, 31(11), 2192-2197.

BS-TuP-9 High-throughput Therapeutic Drug Monitoring of Immunosuppressive Drugs using Tungsten Disulfide-based Laser Desorption Ionization*, Sunho Joh,* *H. Na, J. Son, A. Lee,* Korea Research Instutue of Standards and Science (KRISS), Republic of Korea*; C. Ahn,* Yonsei University, Korea, Korea (Democratic People's Republic of)*; D. Ji,* Yonsei University, Korea*; J. Wi,* Hanbat National University, Republic of Korea*; M. Jeong,* Hanyang University, Korea*; S. Lee,* Yonsei University, Korea*; T. Lee,* Korea Research Instutue of Standards and Science (KRISS), Republic of Korea

Transition metal dichalcogenides are promising candidates for alternative matrix-assisted laser desorption and ionization (MALDI) matrices owing to their excellent physicochemical properties.[1,2] Characteristics of tungsten disulfide (WS_2) such as strong UV absorbance, direct bandgap, low thermal conductivity and high electron mobility are conducive to serve as an effective inorganic matrix; however, its application in mass spectrometry (MS) is rarely reported.[3,4] Here, we present a sensitive time-of-flight (TOF) MS platform by utilizing WS_2 nanosheet-assisted laser desorption ionization (LDI) for quantitative analysis of immunosuppressive drugs in the blood of organ transplant patients. By adopting a micro-liquid dispensing inkjet microarray system, high-throughput analysis of the patient samples with enhanced sensitivity and reproducibility was achieved. To evaluate the performance of our LDI-MS platform, up to 80 cases of patient samples were analyzed and the results were compared with those of liquid chromatography tandem mass spectrometry (LC-MS/MS). The results obtained by inkjet-printed WS_2-assisted LDI-MS were in good agreement with those of LC-MS/MS while being rapid and cost-effective. Our advanced material and method will facilitate therapeutic monitoring of blood samples from a large number of patients for accurate immunosuppressive drug prescriptions.

[1] Kim, Y. K.; Wang, L. S.; Landis, R.; Kim, C. S.; Vachet, R. W.; Rotello, V. M. *Nanoscale***2017**, *9* (30), 10854–10860.

[2] Zhao, Y.; Deng, G.; Liu, X.; Sun, L.; Li, H.; Cheng, Q.; Xi, K.; Xu, D. *Anal. Chim. Acta***2016**, *937*, 87–95.

[3] Choi, W.; Choudhary, N.; Han, G. H.; Park, J.; Akinwande, D.; Lee, Y. H. *Mater. Today***2017**, *20* (3), 116–130.

[4] Joh, S.; Na, H. K.; Son, J. G.; Lee, A. Y.; Ahn, C. H.; Ji, D. J.; Wi, J. S.; Jeong, M. S.; Lee, S. G.; Lee, T. G. *ACS Nano***2021**, *15* (6), 10141–10152.

Keywords: Tungsten Disulfide, Laser desorption ionization, Therapeutic drug monitoring, Nanosheets

BS-TuP-11 Tof-Sims Imaging of Organic and Minerals Matters in Primitive Meteorites*, **Manale Noun,*** Lebanese Atomic Energy Commision, NCSR, Lebanon*; Y. Arribard,* Institut d'Astrophysique Spatiale, Université Paris-Saclay, France*; S. Della-Negra,* IJCLab, CNRS/IN2P3, Université Paris-Saclay, France*; R. Brunetto,* Institut d'Astrophysique Spatiale, Université Paris-Saclay, France*; D. Baklouti,* Institut d'Astrophysique Spatiale, Université Paris-Saclay, France, , France

Introduction:

The primitive organic matter of the chondrites is a witness to the early stage of the Solar System.Their investigations aid in understanding critical issues in astrochemistry and astrophysics. In this work, we present the study of organic and inorganic matters of differently altered CM chondrites (Cold Bokkeveld [1] and Paris [2,3] directly analyzed without any chemical extraction by TOF-SIMS technique [4,5].

Materials and methods:

Millimetric unpolished fragments of the two meteorites were measured using an ION-TOF V mass spectrometer. Areas of 500 µm*500 µm were analyzed using a bismuth clusters beam of 2 µm of spatial resolution. Cleaning with argon clusters was performed systematically prior to the analyses according to an established previous protocol [5].

Results and discussion:

The goal of this research is to understand the effect of the aqueous alteration process, which will lead to a better understanding of the hydrothermal processes in the parent asteroids. The SIMS imaging highlight some differences between the composition of the two meteorites. The Cold Bokkeveled sample shows that the "CN^- and CNO^-" fragments are prevalent throughout the sample and are due to organic compounds. While the Paris meteorite demonstrates that these fragments are only found throughout the matrix and are due to sodium and potassium cyanide salts, as well as nitrogen-rich organic matter. Moreover, the comparison of the "H/C" ratio to the number of carbon in the two meteorites reveals that the Cold Bokkeveld has less hydrogenated fragments and a more aromatic, olefinic and/or cross-linked structure. This relationship between aromatization and aqueous alteration is consistent with previous studies [6].

Conclusion

TOF-SIMS measurements allow to highlight the aromatization and the decrease of aliphatic chains with the increase of aqueous alteration. The application of this analytical approach to various altered chondrites levels permits more comprehension of the asteroid alteration processes.

References:

[1] Rubin A. et al. (2007) *Geochimica et Cosmochimica*, A71(9), 2364-2382

[2] Hewins R.H. et al. (2014*)* Geochimica *et Cosmochimica*, A124, 190-222

[3] Marrochi Y. et al. (2014) *Meteoritics & Planet. Sci.*, 49(7), 1232-1249

[4] Dionnet Z. et al. (2018), *Meteoritics & Planet. Sci.*, 53(12), 2608-2623

[5] Noun M. et al. (2019) *Life*, 9(2), 44

[6] Alexander C.M.O.D. et al. (2014) *Meteoritics & Planet. Sci.*, 49(4), 503-525

BS-TuP-13 Time of Flight Secondary Ion Mass Spectrometry (ToF SIMS) Analysis of Porous Transport Layers for Proton Exchange Membrane Water Electrolyzers*, **Genevieve Stelmacovich,*** *M. Walker,* Colorado School of Mines*; D. Cullen ,* Oak Ridge National Laboratory*; S. Ware, T. Schuler, G. Bender,* National Renewable Energy Laboratory*; A. Paxson ,* Plug Power*; S. Pylypenko,* Colorado School of Mines

As the United States strives to develop a hydrogen-based energy infrastructure, there is a heavy industrial focus on the optimization and scale up of reliable hydrogen production. A promising system for large-scale hydrogen production is the proton exchange membrane water electrolyzer (PEMWE). Unfortunately, there are still major advances that need to be made with both cost efficiency and durability before PEMWE's can be used on a commercial scale. In PEMWE's, the porous transport layer (PTL) contributes to a large percentage of overall cell cost. Due to the harsh operating conditions of the anode, protective coatings are applied to the PTLs, but the use of noble metals leads to cost concerns. Additionally, the degradation of coated PTLs at various operating conditions is not well understood. As the hydrogen production industry continues to try to improve the PTL, and ensure reliable operation of the device over long-term, advanced physicochemical characterization at various stages of fabrication and testing is vital to improve durability and meet cost targets.

Currently, the state-of-the-art characterization technique to analyze PTL's and their respective protective coatings is Focused Ion Beam Scanning Electron Microscope, Scanning Transition Electron MicroscopeEnergy Dispersive X-ray Spectroscopy(FIB-SEM STEM-EDS). This technique is labor and time intensive and only targets a small area of the PTL, thus is an impractical technique to rely on for industrial testing. This talk will introduce ToF SIMS as a promising technique for the characterization of PTLs with focus on protective coatings and interface between coating and PTL. This presentation will highlight the benefits of this technique in comparison to current techniques, as well as discuss challenges with optimization of ToF SIMS for these morphologically challenging samples.

Author Index

Bold page numbers indicate presenter