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Multi-Probe Mass Spectrometry Imaging of *Dictyostelium Discoideum* Cells

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Biological performance at the cellular level is mediated by the chemical environment and surface chemistry. The structural and compositional complexity of biological systems requires the use of "specific and complimentary tools" for a comprehensive understanding of the system counterparts and underlying dynamics. Over the last decades, a common pursuit has been the generation of signature secondary ions from a surface of interest and their separation and identification. In the present work, a combined cluster ToF-SIMS, nanoparticle TOF-SIMS, MALDI-TOF-MS and MALDI-FTMS approach for the characterization of native biological nanodomains will be presented.

In the case of cluster ToF-SIMS, the projectile size and energy dependence on the secondary ion yield will be discussed. In particular, the case of a new generation 100 kV ToF-SIMS probe for the analysis of native biological domains (from single cells to tissue sections) will be shown, where molecular ion signals per impact (~10^3 nm desorption volume) can be increased (up to tens of percent) with the use of high energy, massive gold nanoparticles (e.g., 520 keV Au_{400}^{+4} NP). This recent development, when combined with single event electron detection, makes feasible the generation of sub-micron resolution molecular ion maps (e.g., ~100 nm - 1μm resolution, m/z up to 1500).[1]

The generation of mass spectrometry friendly conditions for the analysis of single cell under physiological conditions will be discussed. For example, we successfully developed mass spectrometry friendly surfaces for cell capture and immobilization. Recent studies have shown the possibility of mapping analyte-specific ion distributions from single cells and developing substrates that enable juxta-positioning of multiple distinct cell types with micrometer-scale resolution. Organizing different cell types into precise spatial configuration is important for tissue engineering and drug screening applications.

An initial set of NP-ToF-SIMS and MALDI-FTMS experiments on model single cells systems showed that the most abundant molecular ions can be observed under 520 keV Au_{400}^{+4} NP single impacts. It is worth mentioning that in single event 520 keV Au_{400}^{+4} NP-ToF-SIMS, the analytical information comes from the top 10 nm and the surface area interrogated over the whole analysis is less than 1% for a field of view of 100x100 μm^2 with 10^6 impacts (assuming an area of emission of $10^2 nm^2$ per impact); notice that under these conditions, surface integrity is preserved (i.e., non-destructive analysis) and no preparation is required. On the other hand, preliminary results suggest that Au_{400}^{+4} NP projectiles can be focused to a 10X10 μm^2 field of view which would permit ~100% surface interrogation over the same analysis time (~10^6 impacts). The enhanced molecular ion emission observed during NP bombardment permits the generation of high resolution molecular ion maps via the localization of the impact site. This approach is impractical with smaller projectiles due to the low secondary ion emission yields (~10^{-4}-10^{-3} ions per impact). The enhanced secondary ion yield per NP impact permits the coupling of NP-ToF-SIMS with TIMS-MS. That is, the high spatial resolution obtained from a single NP impact can be integrated with the structural identification of the desorbed species by the analysis of their size-to-charge

and mass-to-charge ratios.[2]

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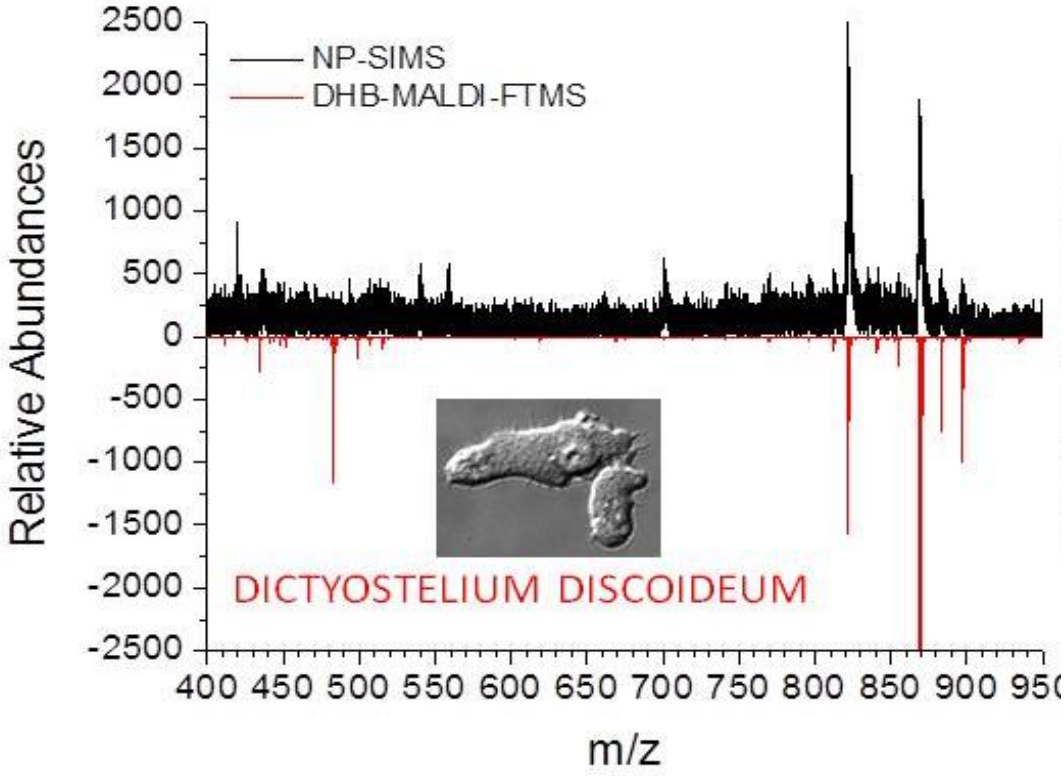

Figure 1. Representative 520 keV Au_{400}^{+4} NP-ToF-SIMS and MALDI-FTMS spectra from a single cell. (obtained in collaboration with Dr. Schweikert group from TAMU)

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