Self-Assembled Gold Nanoparticle Film for Nanostructure-Initiator Mass Spectrometry with Passive On-Line Salt Fractionation

Todd A. Duncombe[1*] (taduncombe@lbl.gov), Paul Adams[1],
Anup Singh[1,2], Trent Northen[1]

[1]Joint BioEnergy Institute, Emeryville, California, USA; [2]Sandia National Laboratories, Livermore, California, USA

Project goals: Sensitive and robust array-based mass spectrometry tools are essential for performing metabolic screens. This work aims at developing a novel analytical platform to perform high-throughput analysis of complex samples using an on-line fractionation process followed by laser desorption ionization mass spectrometry.

Surface Assisted Laser Desorption Ionization (SALDI) is a method of ionization for mass spectrometry that uses a nanostructured medium to absorb energy from an incident laser and transfer that energy onto a target sample. The transferred energy ionizes and desorbs the target sample such that it can be injected into a mass analyzer for the charge to mass ratio of the molecules to be detected. In contrast to Matrix Assisted Laser Desorption Ionization (MALDI), SALDI does not require the addition of matrix ions to facilitate the LDI process. Thus eliminating deleterious 'matrix effects' such as ionization suppression of the molecules of interest, high background, or matrix ions with a similar mass to charge ratio obscuring the detection. SALDI-MS platform that has, in the past, leveraged laser-resonant wet etched-silicon nanostructures and initiator molecules for high sensitivity detection of adsorbed small molecules, lipids, and peptides in LDI-MS. Previously developed, nanostructure-initiator mass spectrometry (NIMS), required fabricating a nanostructured-silicon wafer using hydrofluoric acid etching followed by the manual coating of an initiator molecule. Due to the low-repeatability of both steps – a wide degree variability is observed from one NIMS surface to the next. In this work, we created an improved NIMS platform utilizing fluorinated Au nanoparticles assembled on a surface for the analysis of spotted samples.

We present the self-assembly of fluorinated Au nanoparticle films as a mass-producible fabrication methodology for generating nanostructure-initiator mass spectrometry substrates. The nanostructured surfaces enable the direct high sensitivity detection of peptides (20 femto mol) and other small molecules using laser desorption ionization. Further, through a photolithographic liftoff technique we can realize micropatterned fluorinated Au nanoparticle films. These micropatterns create a discrete wettability patterns, allowing us to passively fractionate hydrophobic molecules of interest from high-salt background environments for robust and predictable mass spectrometry.

References

Northen, T.R., et. al., Clarthrate nanostructures for mass spectrometry, *Nature*, **449**, 1033 (2007).

This work conducted was supported by the US Department of Energy, Office of Science, Office of Biological and Environmental Research, through contract DE-FC02-07ER64494 and through contract DE-AC02-05CH11231, respectively.