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## Elaboration of nanoneedle arrays via nanosphere lithography and single step continuous ICP etching: Application for the detection of Rhodamine 6G by SERS and mass spectrometry.

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Silicon nanostructures like nanoneedle arrays present a huge potential for various applications such as photovoltaic cells [1], information storage [3] and sensing, especially biosensing [4]. Nanoneedles (NNs) are defined as nanomaterials presenting high aspect ratio. Those belong to two main classes: single needles, externally manipulated to contact cells and tissues (near field microscope (AFM), Micromanipulator) or arrays of vertical high aspect ratio nanostructures supported on a substrate. The former encompasses a wide variety of nanostructures including nanowires, nanopillars, porous nanocones, nanotubes, and nanostraws. Variety of materials/dimensions/shapes make each type of NNs having different properties that befit specific sensing needs, that is to say various applications in mechanobiology, nanoelectrophysiology, optogenetic, nanophotonic, transfection/vectorization (drug delivery) [5].

What we suggest here is the development of innovative minimally invasive nanoneedle based platforms which would present two principal abilities (Figure 1). Firstly, to probe the cells without damaging them while capturing biomarkers of interest. Secondly, to use the NNs as a multimodal detection platform which could provide a signal in SALDI-MS<sup>1</sup> and SERS<sup>2</sup> sensing methods. As opposed to MALDI-MS<sup>3</sup>, SALDI doesn't use any organic matrix but is based on an optimized nanostructured surface such as our NNs which could provide better result in terms of S/N ratio. Combining SERS and SALDI-MS is of great interest considering the possibility on one sample to have structural information of molecules from SERS and to identify similar ones looking at their  $m/z$  ratio with SALDI-MS. Several studies made good use of this multimodal detection to distinguish biomolecules and their toxic enantiomers [6] or to improve imaging technics based on these methods [7].

To this extent, we present the fabrication techniques of the NN's. Following the uniform self-assembly of polystyrene particles *via* nanosphere lithography step, a single step continuous ICP etching was achieved. The interest of this lithography method is to reduce the cost and increase the speed of fabrication compared to common lithography based processes. The nanoneedle arrays obtained with this method were then characterized with water contact angle, AFM, SEM and reflectometry measurements. We developed the surfaces adjusting their characteristics by tuning the fabrication's parameters. Indeed, analysis were conducted on Rhodamine 6G as standard molecule and the results obtained with SALDI and SERS were compared to tune the NN properties as well as the deposition methods of R6G. Therefore, we were able to functionalize them by silanization or thanks to electroless metal particles' deposition made of copper, gold, or silver (Figure 2). As said before the platform should present the compatibility for SERS and SALDI but also abilities for cell probing. Therefore, in order to confirm the possibility of intracellular capture of specific biomarkers (peptides, enzymes, proteins) involved in many diseases, we had to assessed the neuronal cell viability after extended interaction with our different functionalized NN arrays.

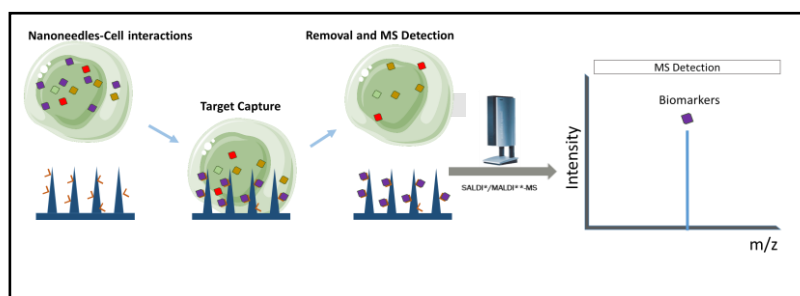


Figure 1: schematic description of the sensing process, left: capture of the target without altering the integrity of the cell, right: analyse of the targets captured by SALDI-MS detection

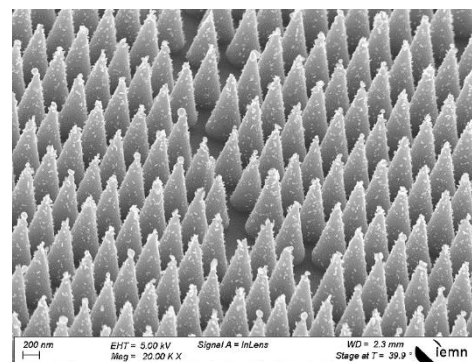


Figure 2: Silver nanoparticles deposited by electroless metal deposition on a nanoneedle array

<sup>1</sup>: Surface Assisted Laser Desorption Ionization - Mass Spectrometry

<sup>2</sup>: Matrix Assisted Laser Desorption Ionization - Mass Spectrometry

<sup>3</sup>: Surface Enhanced Raman Spectroscopy

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