RÉPUBLIQUE FRANÇAISE
Liberté Égalité Fraternité

cnes CENTRE NATIONAL D'ÉTUDES SPATIALES

INTEGRATION OF A NANOSTRUCTURED SENSOR FOR THE ELECTROCHEMICAL DETECTION OF BIOMARKERS : TOWARDS SEARCH FOR LIFE IN SPACE

Marc KELLER [a], Karine MOUGIN [a], Jérôme LAUNAY [b], Delphine FAYE [c], Vincent VIVIER [d], Arnaud BUCH [e], Pierre BAUER [f], Pierre PONTHIAUX [g]

[a] Institut de Sciences des Matériaux de Mulhouse, 15 Rue Jean Starcky, BP2488, 68057 Mulhouse Cedex, France

[b] Laboratoire d'Analyse et d'Architecture des Systèmes, 7Avenue du Colonel Roche, 31400 Toulouse, France

[c] Centre National d'Etudes Spatiales, 16 Avenue Edouard Belin, 31400 Toulouse, France

[d] Laboratoire Interfaces et Systèmes Electrochimiques, 4 Place Jussieu, 75252 Paris Cedex 05, France

[e] CentraleSupelec, 3 Rue Joliot-Curie, 91192 Gif-sur-Yvette Cedex, France

[f] Institut NEEL, 25 Rue des Martyrs, BP166, 38042 Grenoble Cedex 9, France

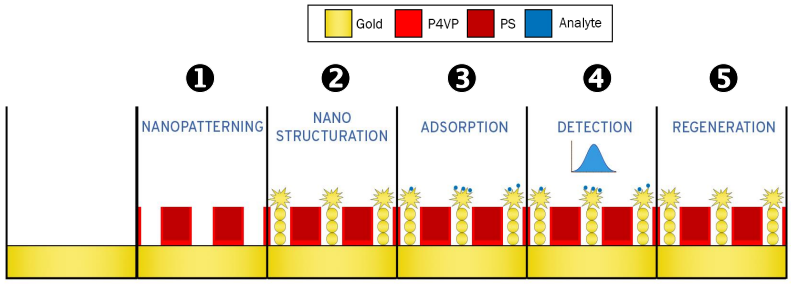
[g] Laboratoire Génie des Procédés et Matériaux, Grande Voie des Vignes, 92 295 Châtenay-Malabry Cedex, France

Abstract and objectives

The search for life on Mars began in 1976 with the launch of the two Viking Landers, which were designed to detect the presence of complex organic molecules. Nowadays, the current scientific and space context needs to develop new microchip detectors that are compact, easy to use, highly sensitive and reactivatable, in order to qualitatively, selectively and quantitatively determine traces of primary organic molecules.

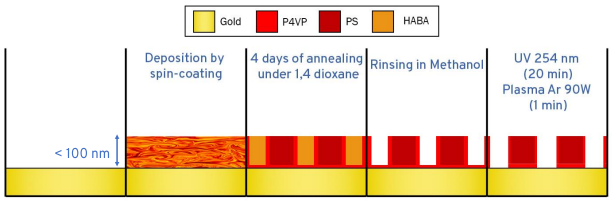
The objectives are :

- Create a nanostructured surface with specific electrochemical and optical properties
- Integrate this sensor into a demonstrator (lab on chip) with a microfluidic system
- Evaluate the microelectrochemical platform
- Validate the concept of this new sensor

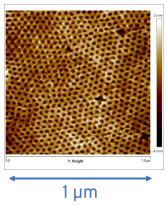


1 Nanopatterning

Chemical process to obtain the nanoporous template



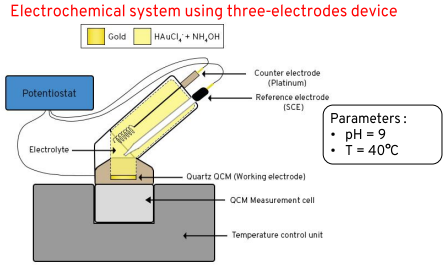
AFM Characterization of the copolymer film



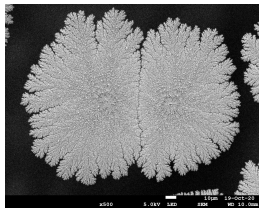
Polymer structuration into hexagonal array of nanopores by controlling the film thickness of the thin coating of PS-B-P4VP

2 Nanostructuration

Electrochemical system using three-electrodes device



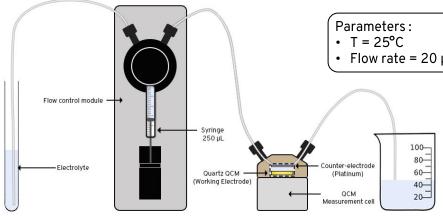
SEM Characterization of flower-like structures



Growth of flower-like nanostructures by electrochemical process : pulsed electrodeposition
Control of the temperature, pH, concentration, kinetics and electrolysis parameters

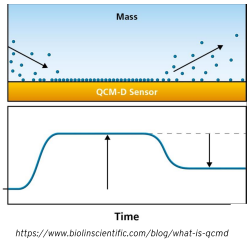
3 Adsorption

Fluidic system using a syringe pump



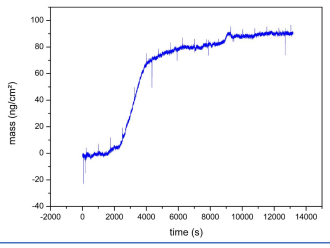
Parameters :
- T = 25°C
- Flow rate = 20 µL/min

Quartz Crystal Microbalance (QCM) principle

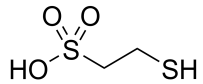


https://www.biolinscientific.com/blog/what-is-qcmd

Adsorption of 10^{-6} M of 2-mercaptoethanesulfonic acid in water



2-mercaptoethanesulfonic acid

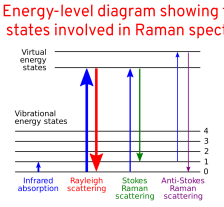


Adsorption of molecules in a fluidic system. Control of the mass adsorbed by controlling different parameters : solvent, temperature, surface cleanliness, flow rate, wettability and physico-chemical properties of the analyte.

4 Detection

Spectroscopic Analysis

Energy-level diagram showing the states involved in Raman spectra



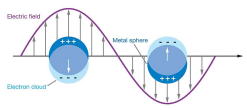
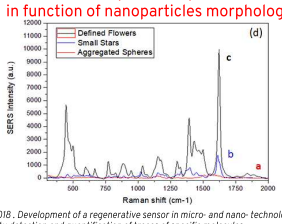
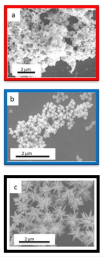


Illustration of the excitation of localized surface plasmon resonance

- Fingerprint of molecules

Detection intensity of Methylen Blue (10^{-7} M) in function of nanoparticles morphology





Bauer, P, 2018 . Development of a regenerative sensor in micro- and nano- technologies for the in-situ detection and quantification of traces of specific molecules.

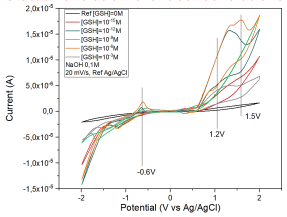
Optical detection of the adsorbed molecules is done by the Raman Spectroscopy
The weak signal can be improved using the plasmonic properties of nanoparticles : the SERS effect

Electrochemical Analysis

- Cyclic Voltammetry (CV) and Differential Pulse Voltammetry (DPV) are sensitive electrochemical technique used for molecule detection especially enantiomers

P. Bauer, K. Mougin, et al. "Synthesis of 3D dendritic gold nanostructures assisted by a templated growth process: Application at the detection of traces of molecules", Langmuir, 36, 37, 11015-11027 (2020)

Detection by Cyclic Voltametry of Glutathione at different concentrations



Electrochemical detection of the adsorbed molecules : using the cylic voltammetry

Conclusions

- **Top-down and bottom up methods** (self assembly of block copolymer (PS-P4VP) and growth of gold nanoparticles) well-established
- Control of the number of **molecules adsorbed**
- Correlation between **optical and electrochemical responses**
- **Regeneration** and **miniaturization** of the sensor

Perspectives

- Test the sensor detection and sensibility on a real environment
- Integration of the sensor
- Detect enantiomer of amino acids

Acknowledgments

- Financial support : CNES and CNRS
- Personal Acknowledgment to the project team

INSTITUT CARNOT MICA · IS2M · cnrs · UNIVERSITÉ DE STRASBOURG ÉTABLISSEMENTS ASSOCIÉS · UNIVERSITÉ HAUTE-ALSACE