Société Française des
Semi-Conducteurs et Oxydes Poreux

6th Scientific SCOPe Days

9-10 November, 2023

http://scope2023.sciencesconf.org

Aula Magna, Place Lemaire, 1
B-1348 Louvain-la-Neuve, BELGIUM

icteam musics incize NETPORE Network on porous semiconductors and oxides ICGM Institut Charles Gerhardt Montpellier UCLouvain

Société Française des
Semi-Conducteurs et Oxydes Poreux

PROGRAMME

6th Scientific SCOPe Days
9-10 November, 2023 - Aula Magna, Place Lemaire, 1, B-1348 Louvain-la-Neuve, BELGIUM

Société Française des
Semi-Conducteurs et Oxydes Poreux

Thursday November 9th, 2023

8:30	WELCOME OF THE PARTICIPANTS
9:00 – 9:15	OPENING OF THE SCOPe DAYS
9:15 – 9:30	PRESENTATION OF NETPORE
9:30 – 10:30	OPENING CONFERENCE (Invited) *"Systematic build of a macroporous model system to test the inherent activity of SCALMS catalysts"* Julien Bachmann – Friedrich Alexander University Erlangen-Nürnberg.
10:30 – 11:00	COFFEE BREAK
11:00 – 11:15	COMMUNICATIONS *«Constrained formation of porous silicon through polymeric masks"* Lisa Monnier, Thomas Defforge, Marylène Vayer, Christophe Sinturel, Gaël Gautier.
11:15 – 11:30	«Effective temperature of porous silicon substrates in LDI-MS in function of etching parameters» Clara Whyte Ferreira, Bastien Cabrera-Tejera, Wendy Müller, Romain Tuyaerts, Gilles Scheen, Yannick Coffinier, Gauthier Eppe, Edwin De Pauw.
11:30 – 11:45	"Functionalization of porous silicon for the detection of dimethyl methylphosphonate (DMMP), a Sarin simulant, by FT-IR and SALDI-MS" Warda Raiah, Mohammed Guendouz, Joël Charrier, Vincent Thomy, And Yannick Coffinier.
11:45 – 12:00	"Increase of the SERS signal from Gold nanospheres in porous Silicon" Clémentine Gevers, Louise Lejeune, Sophie Hermans, Laurent A. Francis.
12:00-13:30	LUNCH BUFFET – POSTER SESSION
13:30-14:30	INVITED CONFERENCE "Porous silicon membranes and their application to indirect bacterial detection» Roselien Vercauteren - VOCSens (srl).
14:30-14:45	COMMUNICATIONS «Effet de l'oxydation sur les propriétés optiques d'un guide d'onde ridge à base de silicium poreux dans le moyen infrarouge» A. Jaafar, S. Meziani, A. Hammouti, P. Pirasteh, N. Lorrain, L. Bodiou, M. Guendouz and J. Charrier.

14:45 – 15:00	“Pencil shape pores in Porous Silicon membrane toward improved efficiency in reverse electrodialysis energy harvesting system” Romain Hanus, Sophie Alicandro, and Laurent A. Francis.
15:00 – 15:15	“2-photon light assisted therapies with porous silicon nanoparticles” Frederique Cunin.
15:15 – 16:00	COFFEE BREAK – GROUP PICTURE
16:00 – 17:00	INVITED CONFERENCE “Post-fab porosification: Challenges and advances” Gilles Scheen - INCIZE - HEPL – UCLouvain
17:00 –18:30	LAB AND FACILITIES VISIT
18:30	End of the day
19:30	GALA DINNER (Hôtel Martins, Louvain-La-Neuve)

Friday November 10th, 2023

8:30	WELCOME OF THE PARTICIPANTS
9:00 – 10:00	OPENING CONFERENCE (Invited) "*Porous silicon-based nanoparticles for boosting cancer antitumor immunity and mitochondria-targeting for reactive oxygen species generation*" Prof. Helder Almeida Santos - University of Helsinki.
10:00 – 10:15	COMMUNICATIONS "*Elaboration of nanoneedle arrays via nanosphere lithography and single step continuous ICP etching. Application for detections of neurodegenerative diseases' biomarkers by mass spectrometry*" P. Moustiez, A. Cournut, C.Whyte-Ferreira, S. Halliez, C. Bich M. Colin, C. Enjalbal, Y. Coffinier.
10:15 – 10:30	"*Study of therapeutic effects of two-photon controlled gene delivery with nanoparticles in uveal melanoma using organoid models*" Emilie Lambert, Sean E. Dunn, Jean-Olivier Durand, Jerome Lacombe, Frederic Zenhausern, Fréderique Cunin.
10:30 – 11:00	COFFEE BREAK
11:00 – 12:00	INVITED CONFERENCE "*Photo/electrooxidation of urea in urine for wastewater treatment and hydrogen production*" Dr. Stephane Bastide - Institut de Chimie et des Matériaux, Paris-Est, ICMPE – CNRS – UPEC.
12:00 – 12:15	COMMUNICATIONS "*Bacterial contamination detection in Water and milk samples with porous Si immunosensor coupled with a rapid catalytic signal amplification*" Divagar Muthukumar, May Naim, Giorgi Shtenberg.
12:15 – 12:30	"*Improvement of OER at Structured Si Electrodes Covered by $Fe_2O_3/IrO_2/TiO_2$ Thin Layers Grown by ALD"* Maxime E. Dufond, Sandra Haschke, Kiseok Oh, Sandrine Zanna, Gabriel Loget, Julien Bachmann, Beniamino Sciacca and Lionel Santinacci.
12:30 – 13:00	"ASSEMBLEE GENERALE" OF SCOPe PRIZE OF THE CONFERENCE AND CLOSING OF THE 5th SCOPe DAYS
13:00 – 14:00	LUNCH BOXES
14:00	DEPARTURE FOR BRUXELLES VISIT *(optional)*

Société Française des
Semi-Conducteurs et Oxydes Poreux

INVITED SPEAKERS

6th Scientific SCOPe Days
9-10 November, 2023 - Aula Magna, Place Lemaire, 1, B-1348 Louvain-la-Neuve, BELGIUM

Société Française des
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Systematic build of a macroporous model system to test the inherent activity of SCALMS catalysts

Prof. Julien Bachmann
Friedrich Alexander University Erlangen-Nürnberg, Germany
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Abstract

In the "supported catalytically active liquid metal solution" (SCALMS) concept, a particularly high activity and longevity of the noble metal catalyst is achieved by using it in a dissolved form, for example as an alloy with a low-melting metal such as gallium. So far, insight into reaction kinetics has been limited by the poor control over the geometry of the metal particles (or droplets) and of the porous support that has been possible so far. We have developed a system designed to enable a systematic experimental approach to studying reaction kinetics in SCALMS systems. Firstly, we have explored methods to synthesize suspended SCALMS particles of well-defined size. Secondly, we have minimized the thickness of the surface oxide layer present on the particles. Thirdly, we have controlled the dewetting of the metallic alloy on planar oxidic substrates. Finally, we have prepared supports on which the catalyst particles can be presented along the walls of straight, cylindrical pores. Here, the transport of gaseous reagents and products, their residence times, and their contact with the metal surface can be adjusted accurately and varied systematically.

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Porous silicon membranes and their application to indirect bacterial detection

Dr. Roselien Vercauteren
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Abstract

In this work, we present the fabrication of porous silicon (PSi) membranes via a robust and repeatable process and their application as optical biosensors for the indirect detection of bacteria via their lysate. Unlike conventional porous silicon biosensors, the selectivity of the presented biosensor does not depend on bio-probes attached to the sensor's surface. Instead, selectivity is achieved by introducing lytic enzymes that exclusively target the desired bacteria, modifying the optical properties of the porous silicon membrane as the resulting bacterial lysate penetrates it, while intact bacteria accumulate on top of the sensor.

The porous silicon membranes are manufactured using standard CMOS-compatible microfabrication techniques and then coated with atomic layer deposited TiO_2. This coating not only acts as a passivation layer but also improves the optical properties of the sensor[1]. The potential of the TiO_2-coated PSi membranes was tested for the indirect detection of *Bacillus cereus*, using the bacteriophage-encoded PlyB221 endolysin as lytic agent. Within a total assay time of 1h30, a sensitivity of 10^3 CFU/mL was achieved. The selectivity and versatility of the detection platform were also confirmed, as well as the detection of *B. cereus* in a complex analyte[2].

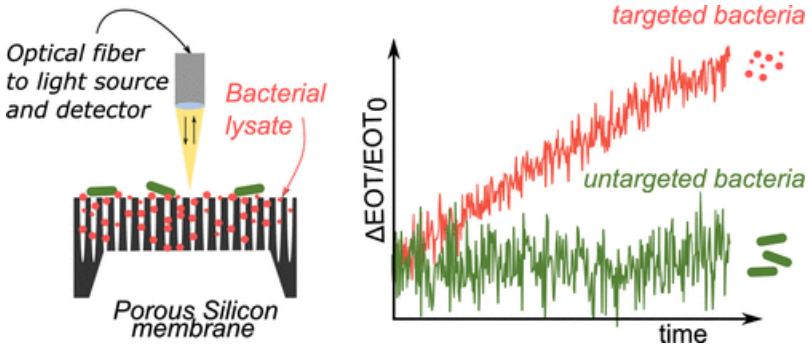

FIG. 1 – *Illustration of the indirect optical detection of bacteria via their lysate on porous silicon membranes: the bacterial lysate penetrates the porous membrane and affects its optical properties while intact bacteria accumulate on top of the membrane. Reproduced from* [2]

(1) Whyte Ferreira, C.; Vercauteren, R.; Francis, L. A. Passivated Porous Silicon Membranes and Their Application to Optical Biosensing. *Micromachines* **2021**, *13* (1), 10. https://doi.org/10.3390/mi13010010.

(2) Vercauteren, R.; Leprince, A.; Nuytten, M.; Mahillon, J.; Francis, L. A. Indirect Detection of Bacteria on Optically Enhanced Porous Silicon Membrane-Based Biosensors Using Selective Lytic Enzymes. *ACS Sens.* **2023**, *8* (7), 2627–2634. https://doi.org/10.1021/acssensors.3c00467.

Société Française des
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Post-fab porosification : challenges and advances

Dr. Gilles Sheen

Abstract

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Porous silicon-based nanoparticles for boosting cancer antitumor immunity and mitochondria-targeting for reactive oxygen species generation

Prof. Hélder A. Santos

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Drug Research Program, Division of Pharmaceutical Chemistry and Technology, Faculty of Pharmacy, University of Helsinki, Helsinki FI-00014, Finland

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Abstract

The development of nanosystems with intrinsic mmunomodulatory effects on macrophage polarization is important for the macrophage-targeted immunotherapy [1]. Moreover, an alternative strategy of choosing photothermal and weak-immunostimulatory porous silicon@Au nanocomposites as particulate cores to prepare a biomimetic nanovaccine can improve its biosafety and immunotherapeutic efficacy for solid tumors [2]. Thus, this lecture is 2-fold: firstly, mitochondria-targeted bovine serum albumins (BSAs) are used to improve the biocompatibility of porous silicon nanoparticulate cores on macrophages (**Fig. 1a**); and secondly, we developed an alternative strategy of comprising simultaneous a photothermal and weak-immunostimulatory effect using porous silicon@Au nanocomposites coated with cancer cell membranes (CCM@(PSiNPs@Au)) to create a nanovaccine (**Fig. 1b**).

We concluded that the porous silicon nanocarriers can efficiently deliver mitochondria-targeted BSA into macrophages to generate mitochondrial reactive oxygen species via the interference with mitochondrial respiratory chains, which can further trigger the downstream signaling transduction pathways for the proinflammatory transition. And, we also demonstrated that the developed nanovaccine, can be used as a photothermal therapeutic agent, which synergizea with additional immunotherapies and significantly inhibiting the growth and metastasis of established solid tumors, via the initiation of the antitumor immune responses in the body and the reversion of their immunosuppressive microenvironments.

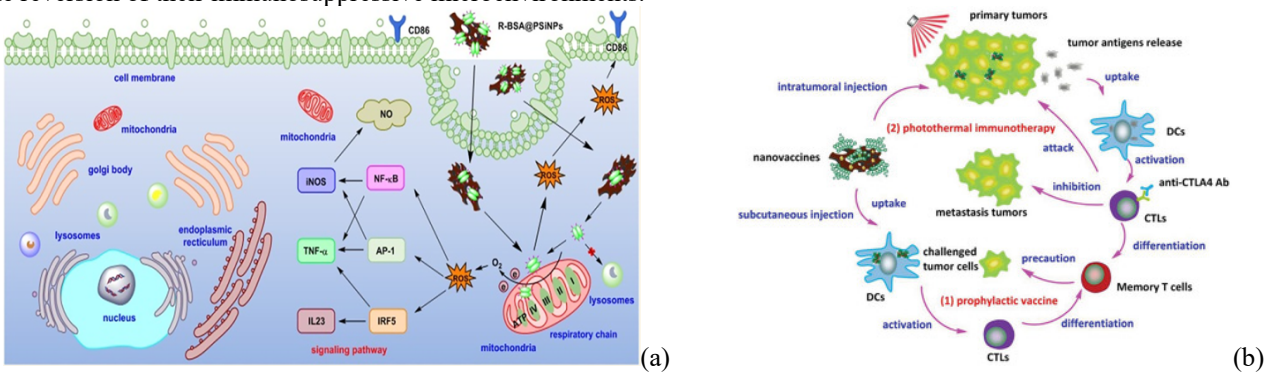

FIG. 1 – *(a) Mitochondria-targeted based porous silicon nanoparticles developed in this study. (b) Porous silicon-based nanovaccine developed in this study.*

[1] Li, J., J. Fan, Y. Gao, S. Huang, D. Huang, J. Li, X. Wang, H. A. Santos*, P. Shen*, B. Xia* (2023). Porous silicon nanocarriers boost the immunomodulation of mitochondria-targeted bovine serum albumins on macrophage polarization. *ACS Nano* 17:1036–1053.

[2] Li, J., D. Huang, R. Cheng, P. Figueiredo, F. Fontana, A. Correia, S. Wang, Z. Liu, M. Kemell, G. Torrieri, E. M. Mäkilä, J. J. Salonen, J. Hirvonen, Y. Gao, J. Li, Z. Luo*, H. A. Santos*, B. Xia* (2022). Multifunctional biomimetic nanovaccines based on photothermal and weak-immunostimulatory nanoparticulate cores for the immunotherapy of solid tumors. *Adv. Mater.* 34:2108012.

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Photo/electrooxidation of urea in urine for wastewater treatment and hydrogen production

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Abstract

The treatment of nitrogen compounds in wastewater at wastewater treatment plants (WWTPs) consumes a lot of energy and has an impact on the environment in the form of nitrate discharges to rivers and N_2O (greenhouse gas) emissions to the atmosphere. WWTP operators are looking for innovative treatments that are more energy efficient and add value to the waste. Since nitrogen is derived from urea, which is mainly present in urine (0.33 mol L^{-1}), electrochemical remediation of urine collected at the source could be a solution to the nitrogen problem in WWTPs.

The aim of our work is to implement a (photo)electrochemical system that allows the degradation of urea (pollutant) at the anode and the production of hydrogen (green fuel) at the cathode, according to the global process:

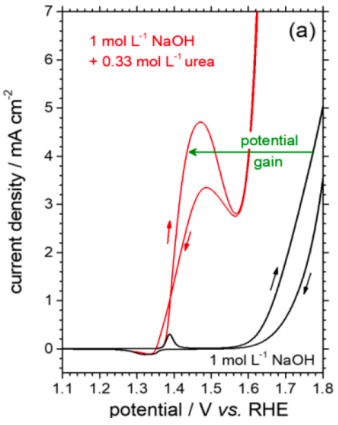
$$CO(NH_2)_2 + H_2O \rightarrow CO_2 + N_2 + 3H_2$$

N_2 is harmless to the environment and H_2 valorizes urea and therefore urine as a waste product. Ni is the best catalyst for this reaction. It allows a gain in potential of several hundred millivolts for H_2 production due to the easier oxidation of urea than water, as shown in Fig. 1a (Ni microelectrode).

In recent years, many studies have been devoted to the evaluation of the electrocatalytic properties of Ni-based catalysts for the electrooxidation of urea [1, 2]. Two main research directions have been followed: nanostructuring of the electrode material to increase the active surface area in different forms (nanowires, nanosheets, nanoribbons, nanoparticles), and the addition of a co-element (e.g., Fe, Co, Mn, Rh) to modify the oxidation potential of urea. In addition, photoelectrochemical systems have also been tested to increase energy savings, using semiconductor-based photoelectrodes, as in our work on hematite (Fe_2O_3) nanorods decorated with nickel catalysts (Fig. 1b) [3].

However, much less work has been done to identify the oxidation products and determine their faradaic efficiencies and selectivities. Only recently have the mechanisms of urea oxidation begun to be elucidated [4].

We will present several aspects of this research area, including our work on the development of 3D electrodes for the electro- and photoelectro-oxidation of urea and on the electrochemical deposition of nickel hydroxide layers (Fig. 1c) to greatly increase the number of catalytic sites. Economic considerations for implementation in WWTPs and potential applications beyond wastewater treatment, such as fuel cells and urea sensors, will also be discussed.



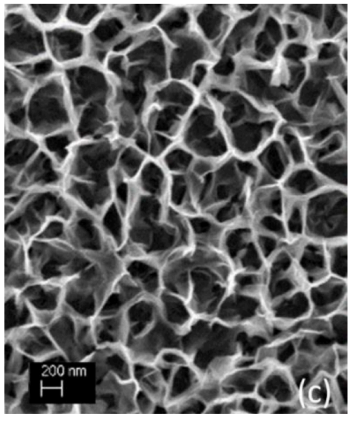


FIG. 1. – *(a) Voltammograms of a Ni microelectrode in NaOH with and without urea; SEM images of (b) a photoelectrode of Fe_2O_3 nanorods decorated with Ni catalysts, (c) an EC-deposited layer of nanostructured $Ni(OH)_2$.*

[1] Li, J., J. Zhang, et J.-H. Yang. (2022). Research progress and applications of nickel-based catalysts for electrooxidation of urea. *International Journal of Hydrogen Energy*, 47:7693-7712.
[2] Urbańczyk, E., M. Sowa, et W. Simka. (2016). Urea removal from aqueous solutions - a review. *Journal of Applied Electrochemistry*, 46:1011-1029.
[3] Rebiai, L., D. Muller-Bouvet, R. Benyahia, E. Torralba, M. L. Viveros, V. Rocher, et al. (2023). Photoelectrocatalytic conversion of urea under solar illumination using Ni/Ti-Fe_2O_3 electrodes. *Electrochimica Acta*, 438:141516.
[4] Tatarchuk, S. W., J. J. Medvedev, F. Li, Y. Tobolovskaya, et A. Klinkova. (2022). Ni-catalyzed urea electrolysis: from nitrite and cyanate as major products to N_2 evolution. *Angewandte Chemie Int. Edition*, 61:e202209839.

Société Française des
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ORAL COMMUNICATIONS

6th Scientific SCOPe Days
9-10 November, 2023 - Aula Magna, Place Lemaire, 1, B-1348 Louvain-la-Neuve, BELGIUM

Constrained formation of porous silicon through polymeric masks

Lisa Monnier [*,**], Thomas Defforge [**], Marylène Vayer [*], Christophe Sinturel [*], Gaël Gautier [**]

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[2] GREMAN UMR 7347, Université de Tours, CNRS, INSA-CVL, 16 rue Pierre et Marie Curie, 37071 Tours, France

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Porous silicon is a nanostructured material resulting from the partial electrochemical etching of crystalline silicon [1]. Constrained formation of electrochemical silicon etching on a silicon wafer was achieved without the use of hard mask which is cost-effective and time-consuming and involves several photolithography and plasma steps [2]. For that purpose, a polystyrene (PS) mask was prepared following a solvent evaporation induced phase separation (SEIPS) in a polymeric blend [3]. The film is perforated with a selective extraction of the other polymer in the blend with a specific solvent, the PS mask exhibits either discrete domains or either perforated continuous area of PS, depending on the composition of the polymer blend. Electrochemical etching through this mask allows to focalize porous silicon on a silicon substrate.

This "all chemical" polymeric mask elaboration opens the ways to constrained porous silicon on a silicon substrate within a large range of shapes and dimensions for applications in microelectronics or optics.

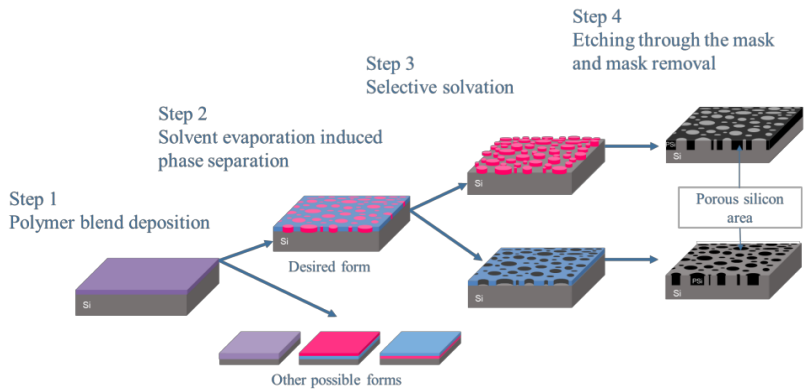

FIG. 1 – Schematic steps for the constrained formation of porous silicon through a polymeric mask structured by SEIPS

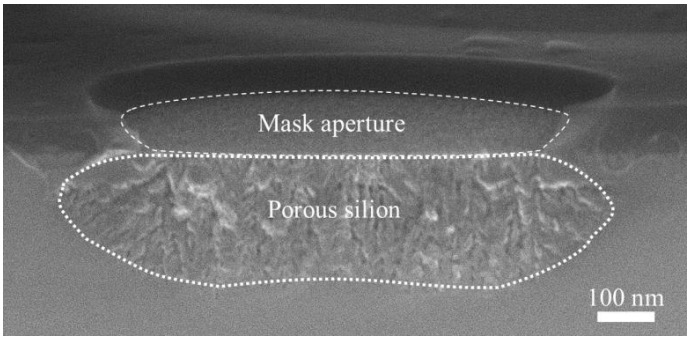

FIG. 2 – SEM image in cross section of silicon doped type P+ (0,01-0,02) after electrochemical etching through a polystyrene mask opened at 42% in an electrolyte of 30%wt hydrofluoric acid and 25%wt acetic acid with an applied current density of J = 164mA/cm2 during 2s

[1] L. Canham, Properties of porous silicon. INSPEC, 1997.
[2] B. Lu, T. Defforge, B. Fodor, B. Morillon, D. Alquier, and G. Gautier, Optimized plasma-polymerized fluoropolymer mask for local porous silicon formation, Journal of Applied Physics, vol. 119, no. 21, p. 213301, Jun. 2016.
[3] A. Vital, M. Vayer, C. Sinturel, T. Tillocher, P. Lefaucheux, and R. Dussart, Polymer masks for structured surface and plasma etching, Applied Surface Science, vol. 332, pp. 237–246, Mar. 2015.

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Effective temperature of porous silicon substrates in LDI-MS in function of etching parameters

Clara Whyte Ferreira*, Bastien Cabrera-Tejera**, Wendy Müller** Romain Tuyaerts*, Gilles Scheen*
Yannick Coffinier***, Gauthier Eppe**, Edwin De Pauw**
*Incize, Ottignies-Louvain-la-Neuve, Belgium
**Mass Spectrometry Laboratory, MolSysResearch Unit, Chemistry Department,University of Liège, Liège, Belgium ***Univ. Lille, CNRS, UMR 8520 - IEMN, Lille, France

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Substituted benzylpyridinium (BP) compounds are used as thermometer ions to characterize porous silicon (PSi) substrates in terms of their effective temperature in LDI-MS. The PSi substrates are produced by electrochemical etching of boron-doped silicon wafers/or surfaces. Porosification parameters are tuned to obtain different morphological features (i.e. porosity, pore size, porous layer thickness).
Surface-Assisted Laser Desorption Ionization Mass Spectrometry (SALDI-MS) is an analytical technique that uses inorganic substrates as assisting materials to improve the desorption/ionisation process.

To be efficient assisting material candidates, these inorganic substrates need strong optical absorption; low heat capacity and large surface area per volume unit. Several substrates have been proposed for SALDI. Among many examples, desorption/ionization on porous silicon (DIOS) is one of the most prominent substrates for SALDI-MS[1].

The exact mechanism behind the desorption/ionization process in these inorganic substrates is not fully understood. In this work, porous silicon (PSi), produced by electrochemical etching, bearing different morphological features is investigated as an inorganic substrate in LDI-MS. Porosifications were conducted using a 3:3:4 HF(49%):IPA:H_2O electrolyte and 10-20 mΩ·cm <100> silicon substrates. The porosification parameters were tuned to yield porosities around 50% and 80%; and thicknesses of 200 nm and 1 µm. The surfaces were then oxidized at 350 °C for 1h under oxygen. Top and cross-section SEM images can be seen in Fig. 1.

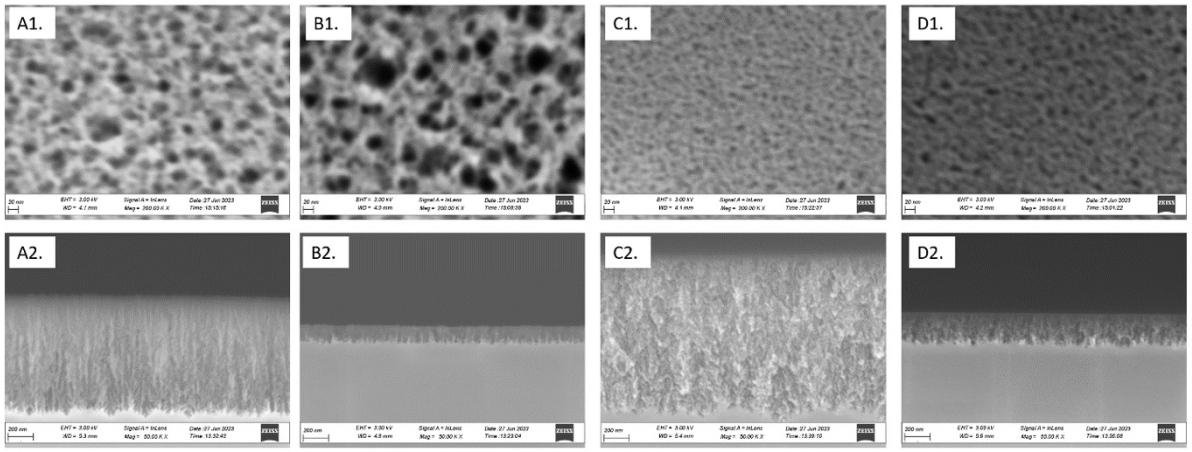

FIG. 1 – Thick (A) and thin (B) PSi obtained with 100 mA/cm2 (porosity around 80%). Thick (C) and thin (D) PSi obtained with 20 mA/cm2 (porosity around 50%).

In order to compare the impact of these different morphologies in SALDI-MS, substituted benzylpyridinium (R-BnPy+) ions are used as model analytes [2]. Experimental conditions are fixed and the internal energies are calculated (E0). The fraction of surviving precursor ions can be obtained from the survival yield (SY)
where I_P and I_F are the intensities of intact precursor and fragment ions, respectively. Finally, the SY values are plotted as a function of the dissociation energy barrier for each thermometer ions. An internal energy distribution can be obtained from the derivative of the sigmoidal curve. By applying a Maxwell-Boltzmann distribution fit, one can extract the thermodynamic temperature (i.e. effective temperature) for the different PSi morphologies.

The results of this study, that will be presented, allowed showing tendencies between porosity and thickness, and survival rate and desorption efficiency, leading the way to a better understanding of the mechanisms, hence the obtaining of optimized substrates for DIOS applications.

[1] Q. Zhu, Z. Wang, Y. Wang, F. Teng, J. Du, S. Dou, and N. Lu, J.Phys. Chem. C, 124, 4, 2450–2457 (2020) [2] C. Collette and E. De Pauw, Rapid Communications In Mass Spectrometry, 12, 165–170 (1998).

Functionalization of porous silicon for the detection of dimethyl methylphosphonate (DMMP), a Sarin simulant, by FT-IR and SALDI-MS.

Warda RAIAH*,**, Mohammed GUENDOUZ**, Joël CHARRIER**, Vincent THOMY*, and Yannick COFFINIER*.

* Institut d'Electronique, de Microélectronique et de Nanotechnologie (IEMN, UMR CNRS 8520), Avenue Poincaré, BP 60069, 59652 Villeneuve d'Ascq, France.

** Institut FOTON (CNRS UMR 6082), Université de Rennes 1, 11b Allée Jean Perrin, 35700 Rennes, France.

Human activities generate a very large quantity of chemical pollutants (dyes, synthetic intermediates, phytosanitary products, persistent organic pollutants (POPs, ex. PFOAS), drugs...). Among these compounds, pesticides are one of the only classes of xenobiotics that are "voluntarily" discharged into the natural environment for agricultural production purposes. Considering the past and current uses, pesticides are represented by more than a thousand active substances, very heterogeneous both in terms of physicochemical characteristics, fate in the environment and their mechanism of toxic action. Most of these pesticides are organophosphorus compounds (OPs). The widespread use of such compounds for several decades has led to their dissemination in all environments of the biosphere (water, soil and atmosphere), with -for some- a long-term persistence. Their chronic toxic effects on the living beings of the terrestrial and aquatic biomass is the result of their accumulation in seeds, plants, fruits but also in the soil, with a potential contamination of drinkable water. In humans, pesticides have direct health effects such as headaches, irritation and abdominal pain, and epidemiological studies have shown the involvement of pesticides in several serious pathologies in people occupationally exposed to these substances, in particular: cancer (prostate cancer, breast cancer, certain hematopoietic cancers such as non-Hodgkin's lymphoma and multiple myeloma), neurological diseases (Parkinson's disease) and reproductive disorders but also during critical periods of fetal development *in utero*. In addition to their agricultural use, some of these organophosphates can be or have been already used as chemical weapons as nerve agent. Once weaponized, they become large-scale weapons of mass destruction. Even if their use was prohibited by the Geneva Protocol (1925), recent events in Syria (1430 victims) or the 1995 attack by the Aum sect in the Tokyo subway (12 dead, 5500 wounded) have shown that these neurotoxins, especially sarin, are still a current threat for populations (bioterrorism) but also for soldiers in the field.

Here, we present recent results on the use of porous silicon for the detection of dimethyl methylphosphonate (DMMP) vapour, a sarin simulant, using both FT-IR spectroscopy and surface-assisted laser desorption ionisation (SALDI) mass spectrometry. SALDI-MS is a matrix-free technique commonly used for the analysis of low molecular weight analytes (< 1000 Da), and porous silicon (pSi) is one of the most successful SALDI substrates due to its high surface area to volume ratio (600 m^2/g), low thermal conductivity and good UV absorptivity. In this study, the pSi surfaces were decorated with CuO particles or TiO_2 coatings to enhance the affinity capture of DMMP and were used as a dual surface, *i.e.* the same pSi surface was able to perform both analyses from the same sample.

Increase of the SERS signal from Gold nanospheres in porous Silicon

Clémentine Gevers*, Louise Lejeune**, Sophie Hermans**, Laurent A. Francis*

*UCLouvain, ICTEAM - ELEN : Place du Levant 3, 1348 Louvain-la-Neuve, BELGIUM
**UCLouvain, IMCN – MOST : Place L. Pasteur, 1/L4.01.03 1348 Louvain-la-Neuve, BELGIUM
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Surface enhanced Raman scattering (SERS) is a widely used method for detecting the presence of biomolecules at low concentrations. This technology increasingly uses porous silicon as a substrate, enabling the generation of 'hotspots' thanks to its rough surface, which are essential for reaching very low detection limits (pM - fM)[1]. However, the impact of the capture of plasmonic nanoparticles, such as Gold ones, in the pores is not yet fully understood. In this work, we used a multiphysics numerical tool (i.e. Comsol Multiphysics [2]) to investigate the properties of Gold nanoparticles embedded in porous Silicon. To reduce the complexity of the analysis, in a first instance we simulated the electromagnetic response of one Gold nanosphere within a single pore (cfr. Fig. 1). The electromagnetic field is exalted because of the effective refractive index of the medium surrounding the nanoparticle, which red-shifts the plasmonic resonance of the nanoparticle to become less affected by the optical absorption, i.e. $Im(\varepsilon)$. Our results indicate that porous silicon is a good substrate for SERS, even when the plasmonic nanoparticles are captured in the pores. As a first result, the enhancement factor of a single gold nanoparticle inside a pore is of the same order of magnitude as a single sphere on a silicon substrate. The electric field enhancement (EF) is 2.83 vs 2.07. This has been computed with the results shown in fig 1 and fig 2.

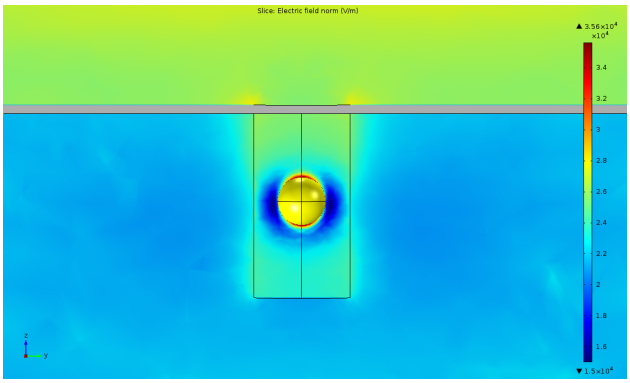

FIG. 1 – Electromagnetic field [V/m] around a gold nanosphere (diameter : 25 nm) within a single pore (radius : 50 nm,

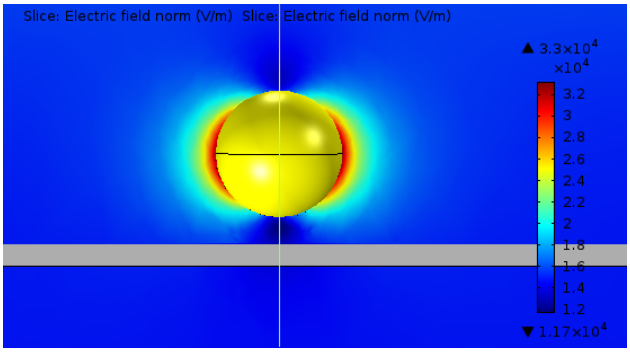

FIG. 2 – Electromagnetic field [V/m] around a gold nanosphere (diameter : 25 nm) on a silicon surface excited by an incident

This work aims thus to analyze the impact of the porous silicon on the increase of the electromagnetic field in the context of the SERS detection.

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Effet de l'oxydation sur les propriétés optiques d'un guide d'onde ridge à base de silicium poreux dans le moyen infrarouge

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Les capteurs optiques intégrés à base de matériaux en silicium poreux (SiP) peuvent détecter efficacement et sélectivement des molécules dans la gamme spectrale du moyen infrarouge (MIR), en exploitant les modes de vibration et de rotation de ces molécules, pour des applications dans le domaine de la santé et de l'environnement.

Dans ce travail, des monocouches de SiP ont été développées par anodisation électrochimique, puis ont été traitées thermiquement sous air pour stabiliser la structure poreuse. Différentes températures de traitement thermique d'oxydation, variant de 300 °C à 900 °C, ont été utilisées afin d'étudier les propriétés structurelles et optiques des monocouches de SiP. La porosité des couches poreuses et le taux d'oxydation du SiP ont été déterminés pour chaque traitement thermique. Les caractérisations optiques ont montré que la transparence des couches de SiP diminue progressivement en fonction du taux d'oxydation. La limite spectrale de transparence est de 8 µm pour une couche non oxydée et elle atteint 5 µm pour une oxydation complète en raison de l'absorption élevée de la silice dans cette gamme spectrale.

Un guide d'onde de type ridge fabriqué à partir de couches de SiP a été ensuite développé par gravure électrochimique suivie d'un processus photolithographique (figure 1-a). Le guide d'onde ridge avec des paramètres précis (porosités, indices de réfraction, dimensions) et non oxydé a permis de guider la lumière dans la gamme spectrale du MIR (de 3.90 à 4.35 µm) avec des pertes optiques d'environ 10 dB/cm (figure 1-b). Une étude de ces pertes optiques a été menée en fonction du degré d'oxydation afin d'identifier l'impact de l'oxydation thermique sur la propagation de la lumière dans le MIR à travers le guide ridge, pour des applications de détection autour de la longueur d'onde de 4.3 µm. Les résultats ont montré que la lumière incidente dans le MIR peut continuer à se propager dans le guide d'onde ridge ayant subi une oxydation partielle à 300 °C ou 600 °C (15 % et 36 % de taux d'oxydation respectivement) avec des pertes optiques d'environ 30 dB/cm et 60 dB/cm respectivement à la longueur d'onde de 4.1 µm (figure 1-b). Cependant, aucune propagation n'a été observée pour le guide ridge en SiP totalement oxydé (à 900 °C) en raison de la forte absorption de la silice à cette même longueur d'onde.

Malgré l'absorption de la silice dans le MIR, nous considérons qu'un guide d'onde en SiP pré-oxydé restera très sensible et présentera une faible limite de détection grâce à sa structure poreuse, qui offre une grande surface d'interaction entre la lumière transmise et les molécules à détecter. Des études sont actuellement en cours pour caractériser optiquement les guides non oxydés et pré-oxydés en fonction de la concentration de CO_2 infiltré dans les pores.

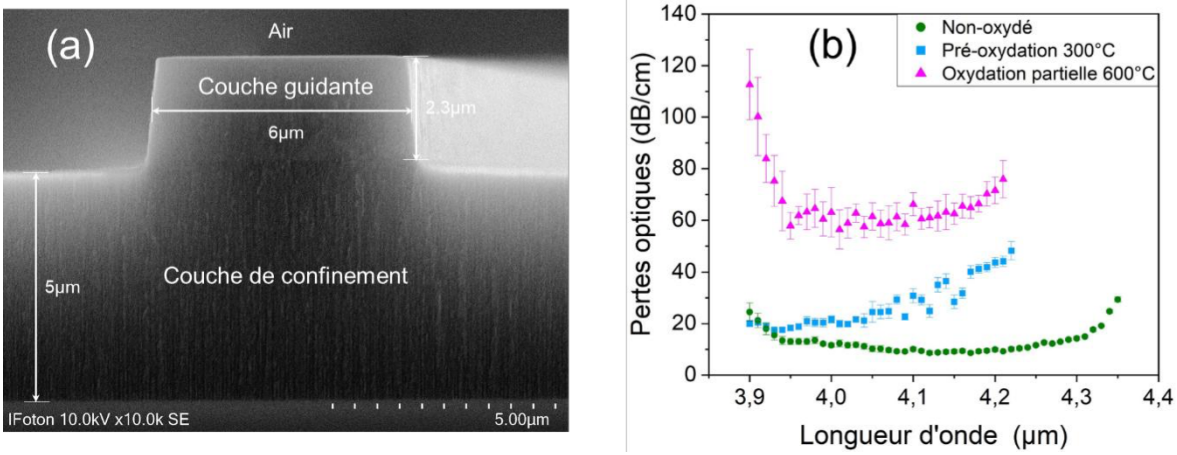

Figure (1) : Image MEB de la vue transversale d'un guide d'onde ridge à base de SiP développé par gravure électrochimique suivie d'un processus photolithographique (a) ; Pertes optiques pour le guide ridge en fonction du traitement d'oxydation dans la gamme du MIR (b).

Pencil shape pores in Porous Silicon membrane toward improved efficiency in reverse electrodialysis energy harvesting system

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Reverse electrodialysis (RED) principle convert saline gradient of electrolyte solutions into electrical power thanks to ion-exchange membranes, as illustrated in Figure 1 [1]. Although, the energy densities currently reached (0.6 Wh/L) are still low compared to the common lithium battery (200-500 Wh/L), RED could meet the energy needs of low-power Internet-of-Things nodes (0.5 mW – 10 mW) and be directly integrated in silicon technologies [1].

In this view, inorganic nanostructured materials have attracted an increasing interest as ion-exchange membranes [2] due to their potentially higher ionic selectivity for an improved efficiency. This higher selectivity results from the overlapping of the electrical double layer (EDL) in the nanostructure of the membrane and RED processes using such membranes are called nano-fluidic reverse electrodialysis (nRED). Porous silicon (PSi) is a good candidate for nRED membranes as its structural attributes are controllable during the multiple fabrication processes, *i.e.*, dry and electrochemical etching, and it is one common material in the integrated semiconductors industry [3].

Currently, research have only studied membranes with cylindrical-shape pore and have shown that, on one hand, narrow pores show good ionic selectivity but higher resistivity and the other hand, larger pores will present lower selectivity and resistivity, resulting in both cases in lower power density. PSi with such pore shape has already been studied in a previous study (0.21 mW/m^2 in 10 mM *vs.* 1 mM NaCl solutions) but the advantages of PSi are yet to be investigated [4]. As an alternative, conically shaped pores (cfr. Figure 2) have been demonstrated to give higher efficiencies due to the trade-off between the good ionic selectivity from small pores and the low ionic resistance of the large pore and have been demonstrated to give higher efficiencies [5,6], but have only been done on single-pore polymer membranes and not silicon.

In this work, we have fabricated PSi membranes with various pore shapes, such as conical and pencil shapes (cfr. Figure 2), by monitoring the current density applied during the electrochemical etching steps on heavily *p*-doped silicon substrates. The SEM images indicate a reduction of the pore size along the thickness of the membrane. Because the EDL overlap depends on the pore size and the ionic concentration, and so the strength of the selective property, better performances are seen when the small end of the pore is exposed to the lowest ionic concentration. This asymmetry is experimentally observed by I-V tests (cfr. Figure 3), while it is absent for cylindrical pores. Furthermore, a comparison with the latter membrane indicates a greater power density of 1.32 mW/m^2 for the pencil shape PSi membrane.

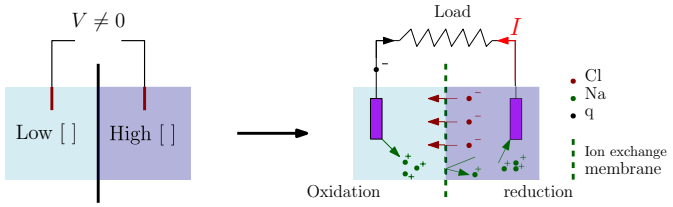

Figure 1: Electrochemical potential between two saline solutions (left) converted in electricity with RED (right)

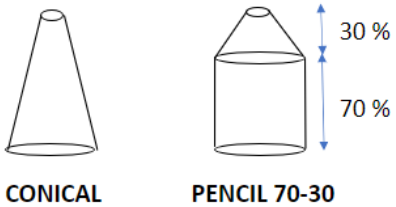

Figure 2: conical pore shape and pencil shape pore

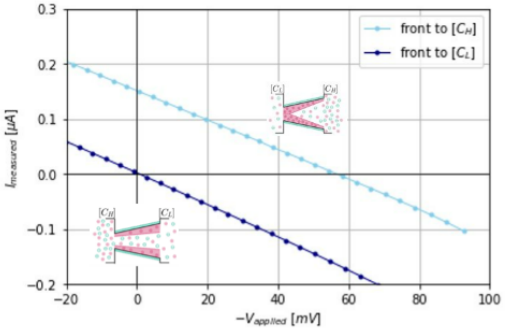

Figure 3: I-V curves for a conical membrane with concentrations at 1 mM and 0.1 mM

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2-photon light assisted therapies with porous silicon nanoparticles

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Local therapy is indicated to overcome the intrinsic biological resistance of certain incurable malignancies, leading to failure of conventional treatment approaches. We aim at developing biodegradable anti-cancer materials based on mesoporous silicon to be used for the local treatment of cancer. Porous silicon nanostructures are bioresorbable in vivo. In addition they can be excited by near infrared 2-photon excitation light offering possibilities for phototherapies, and for light triggered treatment. We will present simple photosensitizer/porous silicon nanoparticle systems based on a porphyrin derivative covalently attached to the nanoparticle and demonstrate imaging and photodynamic therapy under two photon excitation (TPE) conditions. A new mechanism of siRNA delivery and gene silencing in cells upon TPE will be also presented. The development of photoactive porous silicon nanostructures functionalized with organic ligands for applications in imaging, nucleic acids and drug delivery will be described [1,2].

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Elaboration of nanoneedle arrays via nanosphere lithography and single step continuous ICP etching. Application for detections of neurodegenerative diseases' biomarkers by mass spectrometry

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Silicon nanostructures like nanoneedle arrays present a huge potential for various applications such as photovoltaic cells [1], sensors [2], information storage [3] to name a few. 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) [4].

What we suggest here is the development of new, minimally invasive nanoneedle based plateforms for monitoring living cells by leveraging the ability of NNs to access the cell cytoplasm and to get new insights in the understanding of biochemical processes occurring within cells (Figure 1). As a proof of concept, we want to assay the state of intracellular tau in brain cells. Specific modifications and conformational changes of tau are features associated to a group of neurodegenerative disorders called tauopathies and including Alzheimer's disease (AD). Therefore, assaying intracellular tau state in living cells could allow a better understanding of pathophysiological mechanisms involved in AD and other tauopathies but also be used as a biomarker per se. Of note, extracellular deposition of Aβ peptides is another feature of AD. 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. The purpose of these NNs platforms is to combine them with SALDI-MS1 detection; as opposed to MALDI-MS2, this technique doesn't use any matrix but is based on an optimized nanostructured surface such as our NNs which could provide better result in terms of S/N ratio. With that in mind, we developed the surfaces adjusting their characteristics by tuning the fabrication's parameters. Moreover, we were able to functionalize them by silanization or also thanks to electroless metal deposition such as copper, gold, silver (Figure 2) or platinum. SALDI tests were accomplished simultaneously with SERS analysis to be able to confront the results. Finally, we obtained the first results of the effect of the interaction between the needles and primary neural cells in terms of cell viability.

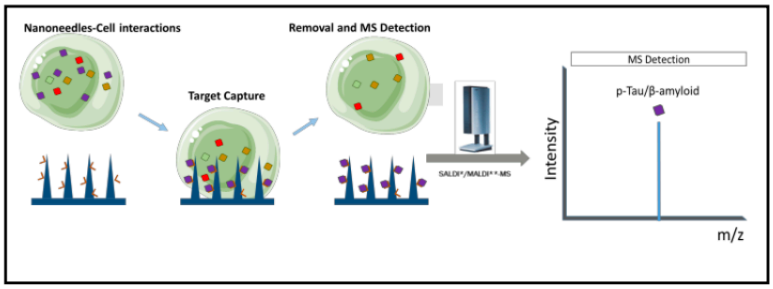

Figure 1: schematic description of the sensoring process, left: capture of the target without altering the integrity of the cell, right: analyse of the targets captured by SALDI-MS detection

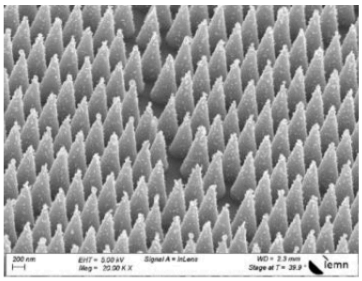

Figure 2: Silver nanoparticules deposited by electroless metal deposition on a

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[1]: Surface Assisted Laser Desorption Ionization - Mass Spectrometry [2]: Matrix Assisted Laser Desorption Ionization

We acknowledge the University of Lille, CNRS and ANR grant NanoIntra ANR-19-CE09-0030. This work was also supported by the French RENATECH network (French national nanofabrication platform).

Study of therapeutic effects of two-photon controlled gene delivery with nanoparticles in uveal melanoma using organoid models

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Porous silicon nanoparticles (pSiNPs) possess a set of unique properties, particularly bioresorbability, biocompatibility, intrinsic photoluminescence as well as favorable porosity for encapsulation purposes, and applications in the biomedical field [1]. The porous structure of pSiNPs provides a large specific surface area for grafting a wide range of molecules, as well as for loading them with drugs and nucleic acids[2]. Photoluminescence properties of pSiNPs, enable light-triggered drugs and nucleic acids release under biphotonic activation in the near infrared, using a photosensitizer such as a cationic porphyrin [3][4]. In this project, pSiNPs were prepared and chemically fonctionalized to vectorize siRNA to melanoma cancer cells. Calibrated pSiNPs were synthesized by anodization and cationic porphyrin was grafted to their surface in order to efficiently complex siRNA within the pores of pSiNPs. The physico-chemical properties of the pSiNPs were characterized at each step of their preparation and functionalization. Cytotoxicity and internalization were carried out on uveal melanoma cell lines.

Tables and Figures:

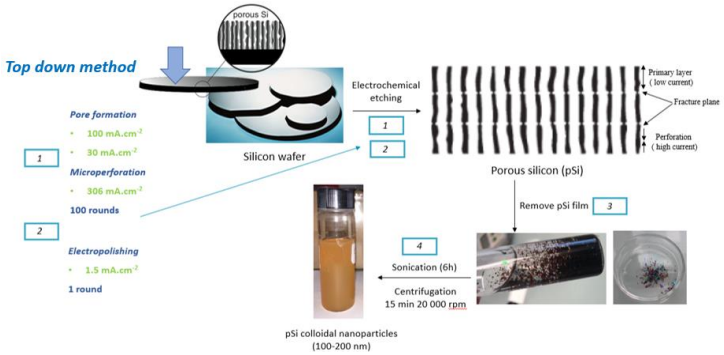

FIG. 1 – *Synthesis scheme of porous silicon nanoparticles.*

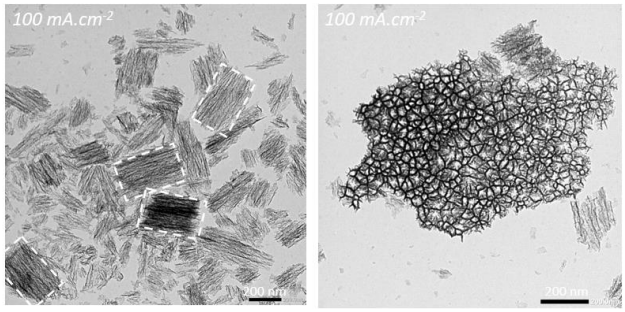

FIG. 2 – *TEM images of porous silicon* .

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Bacterial contamination detection in Water and milk samples with porous Si immunosensor coupled with a rapid catalytic signal amplification

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Rapid, facile and sensitive detection of water-borne pollutants is crucial to safeguard public health. Herein, a miniaturized biosensing platform based on porous silicon (p-Si) interferometer was designed to detect *Escherichia coli (E. coli)* contamination in a rapid and reliable manner. An indirect immunoassay followed by a simple syringe filtration was adapted to exclude the unreacted antibodies tagged with horseradish peroxidase (HRP) from the bacterial suspension while assessing the residual immuno-entities by the optical transducer. The quantification of minute *E. coli* concentrations was achieved by HRP moieties' biochemical activation and real-time monitoring of the reaction products infiltration into the porous nanostructure by alternating reflectance spectra. The developed bioassay depicted high sensitivity against target microorganism detection, as low as 2 CFU mL^{-1} and a linear response of 10^1 -10^5 CFU mL^{-1}. Furthermore, the selectivity was tested using common interfering pathogens, *i.e.*, *Listeria monocytogenes, Salmonella enterica* serovar Typhimurium, *Staphylococcus aureus, Staphylococcus epidermidis* and *Bacillus cereus,* which resulted in satisfying output. Finally, the potential applicability of the developed platform for real-life scenarios was interpreted with respect to the standard culture plate approach while depicting recovery values of 92-114% in ground, irrigation and river water, as well as staple food samples (raw and pasteurized milk). Overall, the miniaturized p-Si scaffold can be utilized for various emerging applications with pathogenesis relevance assessment conducted at on-site conditions.

Keywords: biochemical immunoassay, biosensor, *Escherichia coli*, porous silicon, rapid assay

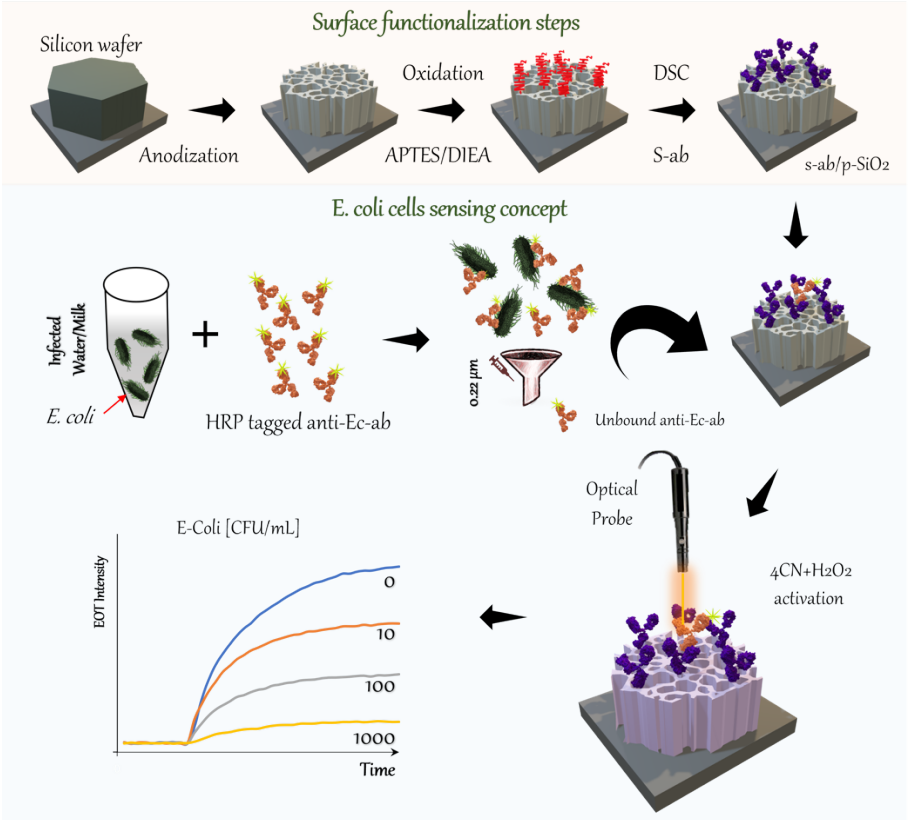

Fig. 1 Schematic representation of the preparation of p-Si immunosensor and detection process

Improvement of OER at Structured Si Electrodes Covered by $Fe_2O_3/IrO_2/TiO_2$ Thin Layers Grown by ALD

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Due to its sluggish kinetics, photooxidation is the limiting reaction of water photosplitting. It has therefore attracted numerous research investigations. Since no semiconductor exhibits all required properties, it is necessary to combine various materials to build efficient photoanodes. Silicon is interesting because it absorbs light in the visible range, it exhibits a long photocarrier lifetime, but it easily corrodes in KOH. Conversely, Fe_2O_3 has a wider bandgap (≈ 2 eV), a very short carrier lifetime but it shows a good stability in the electrolyte. It could therefore be valuable to associate those materials. In addition, surface structuring has already demonstrated its interest for improving the photoelectrodes' performance. In the present work, we report the effect of the geometry of structured Si surfaces coated by successive functional layers ($Fe_2O_3/IrO_2/TiO_2$) grown by atomic layer deposition (ALD).

A simple tow-steps surface structuring (photoelectrochemical and chemical etching) leads to two different geometries: Si macropores (SiMP) and Si nanospikes (SiNS). By tuning the morphology of the SiMP and SiNS (Fig. 1a,b), their light absorption and active area are drastically enhanced as compared to a plane Si surface. Since bare Si cannot be directly used as photoanode, ALD is used to coat those tortuous surfaces with protective and active layers. Thin Fe_2O_3 layers are firstly grown onto Si and their photoelectrochemical efficiencies are compared. Thermal treatments have also been carried out to possibly improve the charge generation within the oxide layer. Finally, an ultrathin IrO_2 layer (< 1 nm) is deposited as co-catalyst. Since IrO_2 is not sable in alkaline medium, the electrode is encapsulated in a protective TiO_2 film (< 1 nm). Though the onset potential for water oxidation is slightly anodically shifted, such photoanode exhibits high performance and satisfying stability (Fig. 1c).

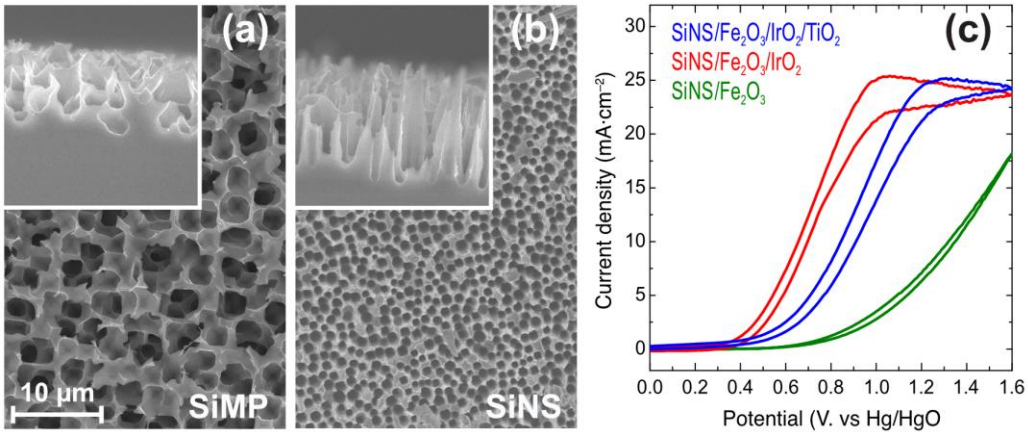

FIG. 1 – SEM top views and cross sections of (a) SiMP and (b) SiNS. (c) Cyclic voltammograms of SiNS covered by the different oxide layers under white light illumination in 1M KOH.

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Contrôle des dimensions de nanoparticules de silicium poreux

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Depuis plus d'une vingtaine d'années, les nanoparticules de silicium poreux sont étudiées comme matériau hôte pour la délivrance médicamenteuse [1]. Le silicium poreux – biodégradable – se dissout progressivement dans le milieu biologique et libère ainsi les principes actifs emprisonnés dans la porosité. Auparavant, la taille réduite des particules leur a permis de passer les barrières biologiques pour parvenir à la zone à traiter. La taille des particules est donc l'un des principaux paramètres dans la réussite de la délivrance médicamenteuse. Il est donc nécessaire d'adapter le procédé de synthèse afin d'optimiser la quantité de nanoparticules poreuses de taille définie.

L'objectif ici est de proposer une méthode innovante de synthèse de nanoparticules de silicium permettant à la fois de produire des objets de même taille mais également de forme similaire [2]. Cette méthode combine deux techniques de gravure du silicium : la voie électrochimique pour produire un film mince de silicium poreux et la voie chimique assistée par métal pour former des nanofils au travers du film mince préalablement obtenu (cf. fig. 1). Les nanofils sont ensuite détachés du substrat silicium et cassés par ultrasons (cf. fig. 2). Les nano-batônnets (nanofils cassés) ainsi obtenus sont ensuite séparés en taille par centrifugation. Au final, cette méthode permet de contrôler deux voire les trois dimensions de l'objet synthétisé avec un rendement supérieur aux méthodes traditionnellement employées.

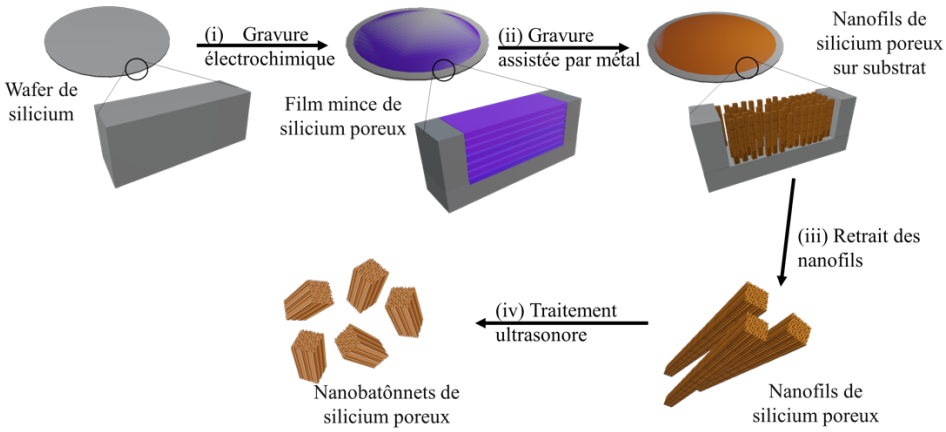

FIG. 1 – *Principe de fabrication de nano-batônnets de silicium poreux.*

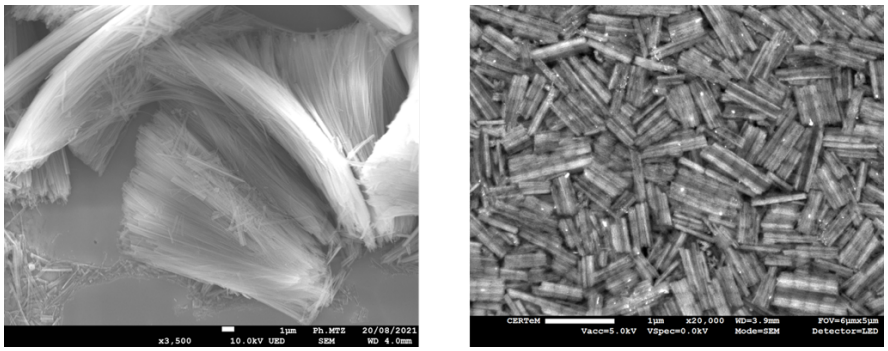

FIG. 2 – *Images MEB de nanostructures poreuses (à gauche) nanofils de silicium poreux détachés et (à droite) nano-batônnets poreux.*

[1] Anglin, E. J., Cheng, L., Freeman, W. R., et Sailor, M. J. (2008). Porous silicon in drug delivery devices and materials. *Advanced drug delivery reviews*, 60:1266-1277.

[2] Chaix, A., Griveau, A., Defforge, T., Grimal, V., Le Borgne, B., Gautier, G., et Eyer, J. (2022). Cell penetrating peptide decorated magnetic porous silicon nanorods for glioblastoma therapy and imaging. *RSC advances,* 12:11708-11714.

Development of a new substrate for rapid and selective detection of pathogens by Raman spectroscopy

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Antimicrobial resistance (AMR) is emerging as a complex and multifactorial issue for global public health [1]. One of the parameters on which it is possible to play is the improvement of rapid diagnosis. In this project, we propose the development of a new biosensor using Surface Enhanced Raman Spectroscopy (SERS) as detection method. The substrate consists of a structured porous silicon membrane acting as a size filter [2] decorated with shape controlled plasmonic nanostructures (Au, Ag, Cu) playing a key role in the RAMAN signal enhancement, in combination with a RAMAN-active molecular probe [3].

In this work, gold nanoparticles of various morphologies (spherical, branched and rods) and of different sizes were synthetized and their localized surface plasmon resonance absorption band characterized by UV-vis spectroscopy (FIG. 1). The first tests on the SERS effect of these gold nanostructures were performed on flat glass substrates, using methylene blue (MB), a colored organic molecule, as a classical RAMAN probe. This allowed us to prove their efficiency in exalting the RAMAN signal under simplified conditions (Fig. 2). The SERS effect was more pronounced when using nano-rods, followed by nano-stars than nano-spheres, due to known influence of anisotropy and spikes of the nanostructures on increasing locally the electrical field generated by the plasmon effect. The next steps will involve surface functionalization and immobilization onto porous silicon substrates that could be used as filtration membranes during analysis of bacteria-containing media.

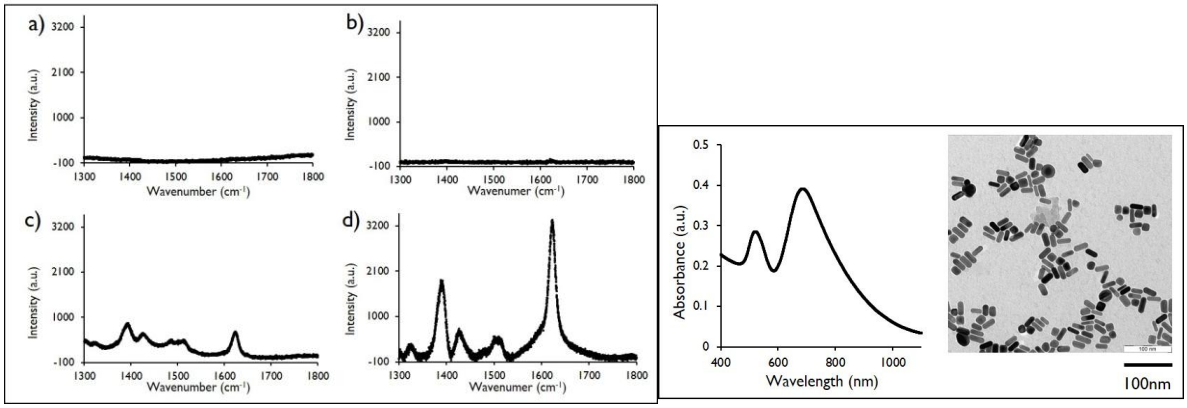

FIG.1 – *Left: Evolution of UV-vis absorption of a suspension of gold nanorods between 400 and 1100 nm. Right: TEM image of the corresponding batch of gold nanorods.*

FIG 2 – *a) Raman spectrum of MB in water (5 10^{-5} mol/L), b,c,d) SERS spectra of MB taken in the same conditions than a) in the presence of gold b) nano-spheres, c) nano-stars, d) nano-rods. All Raman spectra were recorded with a laser source at 633 nm.*

References:

[1] Prestinaci, F., Pezzotti P., Pantosti A. (2015). Antimicrobial resistance: a global multifaceted phenomenon.

Pathogens and Global Health, 109, 7.

[2] Vercauteren, R., Leprince A., Mahillon J., Francis, L.A. (2021). Porous Silicon Biosensor for the Detection of

Bacteria through Their Lysate. Biosensors, 11(2), 27.

[3] Zhou, Y., Lu, Y., Liu, Y., Hu, X., Chen, H., (2023). Current strategies of plasmonic nanoparticles assisted surface- enhanced Raman scattering toward biosensor studies. Biosensors and Biolectronics, 228, 115231.

Effects of N-sources on TiN thin films grown by Plasma-Enhanced Atomic Layer Deposition

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This work consists of optimizing TiN plasma-enhanced atomic layer deposition using two different N-sources: NH_3 and N_2. In addition to maximizing the growth per cycle (GPC) and to shorten the deposition duration, comprehen- sive in and ex situ physicochemical characterizations give valuable information about the influence of the N-source nature, their dilution in Ar and the plasma power on layer's final properties. N_2 and NH_3 dilutions within Ar are ex- tensively investigated since they are critical to decreasing the mean free path ( ) of plasma-activated species. A 1:1 gas ratio for the N-sources:Ar mixture associated to low flows (20 sccm) are optimal values for achieving highest GPCs (0.8 Å/cycle). Due to lower reactivity and shorter of the excited species, N_2 plasma is more sensitive to power and generator-to- sample distance, this contributes to lower conformality than with NH_3 plasma (Fig. 1). The resistivity of the initial amorphous films was high (≥ 1000 μΩ·cm) and were significantly reduced after a thermal treatment (≤ 400 μΩ·cm). This demonstrates clearly the beneficial effect of the crystallinity of the film conductivity. Though N_2 process appears slightly slower than NH_3 one, it leads to an acceptable film quality. It should be considered since it is non-harmful and the process could be further improved by using a reactor exhibiting an optimized geometry.

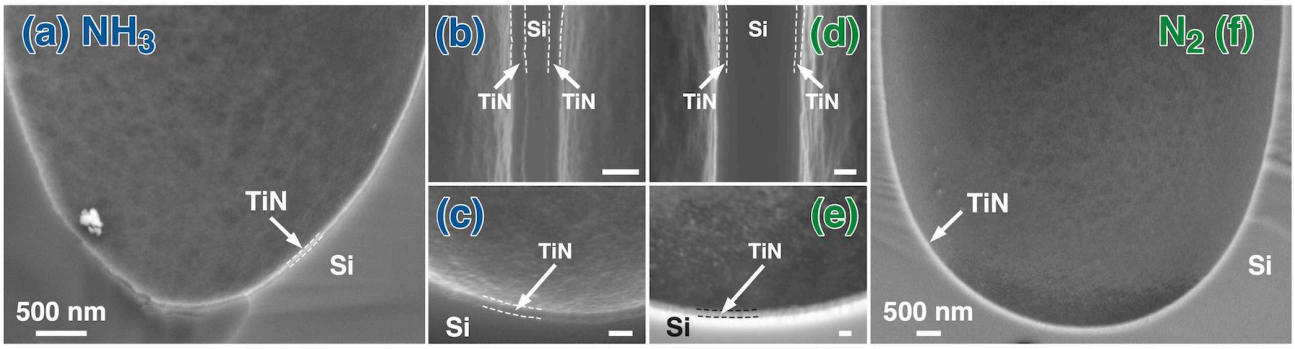

FIG. 1 – *SEM cross sections of porous Si coated by TiN films: (a,b,c) pl-NH_3 and (d,e,f) pl-N_2. (a,f) show general views of pore tips while (b,e) and (c,d) show high magnification images of a single wall at half depth of the pore and at the pore tips, respectively. Scale bars in (b,c,d,e) correspond to 100 nm. Expected 50 nm-thick TiN layers grown at T_{ALD} = 200°C.*

Ultrathin TiO_2 coating of nanostructured porous silicon towards the fabrication of electrodes for artificial photosynthesis applications

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Artificial photosynthesis (AP) is the mechanism allowing to perform CO_2 reduction into fuels (mainly alkanes) thanks to water and solar energy. Although works conducted to improve the selectivity (ability to direct the reaction to yield a particular product), stability (lifetime of the catalyst) and activation (ability to increase the rate of the desired reaction), no industrially viable systems are available at the present date [1]. Efforts to make commercial, circular and scalable systems must be made.
We present the fabrication of electrodes based on an electrochemically etched porous silicon (PSi), coated by atomic layer deposited (ALD) titanium dioxide (TiO_2), a photocatalyst. The porous structure was observed by SEM and we ensured that ALD allowed to deposit the catalyst down to the bottom of the pores using EDX. PSi has proved to be an interesting material for AP applications thanks to its large specific surface area and low reflectivity in the visible. However, it is prone to photo-oxidation, leading the photoelectrochemical cells to be inefficient as the charge transfer becomes impossible. We demonstrate that a TiO_2 layer as thin as ~2.4 Å, whose composition was analyzed by XPS, is thick enough to prevent silicon's oxidation when exposed to water. The passivation efficiency was measured by following during 29 days the Si-O-Si band evolution using FTIR spectroscopy while exposing coated and uncoated samples to water. In addition, the wettability of the samples did not change after functionalization. Finally, photocatalytic degradation rates were significantly increased (by 50% on average) for 10 nm TiO_2 ALD-coated porous silicon samples compared to natural degradation. Interestingly, the thinnest layers (2.4 Å) also showed enhanced catalytic kinetics at short times (t < 40 min) FIG. 2.

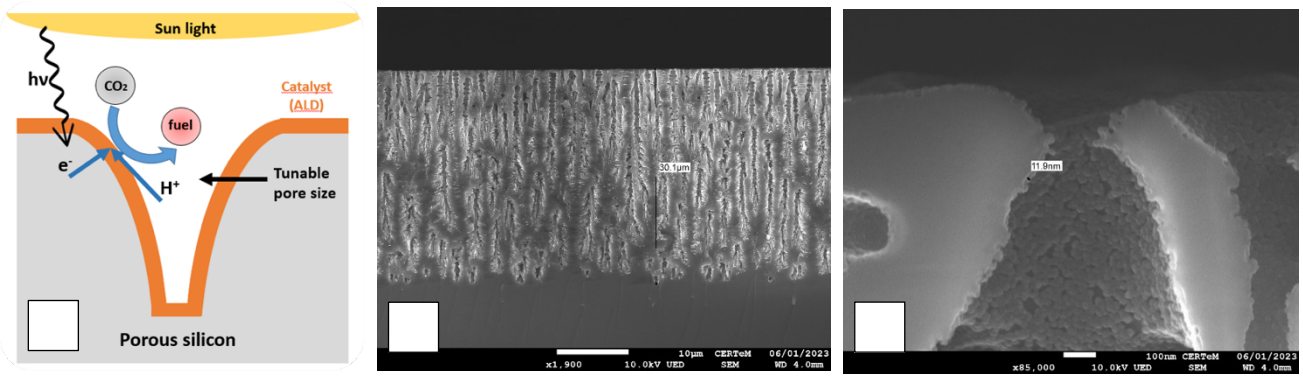

FIG. 1 – *a) Graphic of a cell b) SEM images of a sample showing the overall geometry of the macroporous silicon layer c) details of the TiO_2 layer at the top of the pores.*

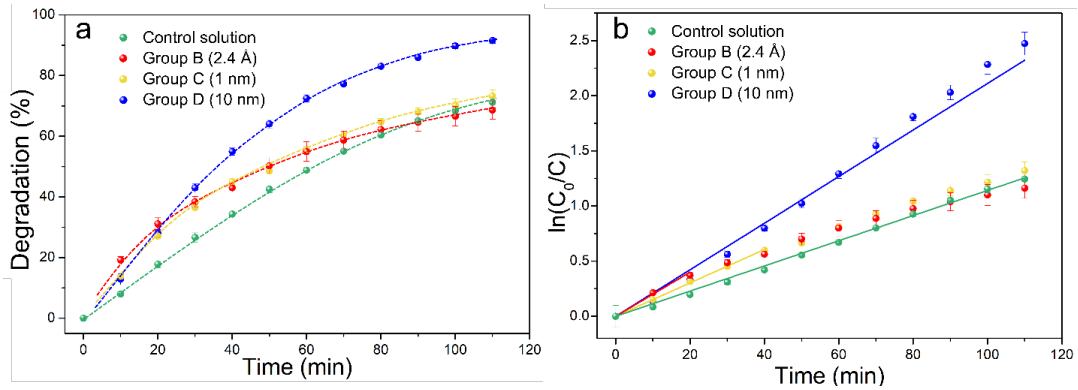

FIG. 2 – *a) Degradation rates of group B, C and D samples and control solution containing only Methylene blue (MB). b) Plot of the MB degradation in logarithmic scale as a function of time.*

[1] Kim, Sungsoon, et al. "Artificial photosynthesis for high-value-added chemicals: old material, new opportunity." Carbon Energy 4.1 (2022): 21-44.

Synthèse d'électrodes de supercondensateur à base de nitrure de titane / silicium poreux

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Les dispositifs supercondensateurs utilisent principalement le principe de stockage de charges électriques à l'interface électrode|électrolyte. La surface spécifique des électrodes tient donc un rôle primordial dans les performances des supercondensateurs. Dans ce contexte, le silicium poreux est un candidat particulièrement intéressant car il allie une surface spécifique élevée et une facilité à la miniaturisation des dispositifs en utilisant les procédés de microélectronique [1]. En revanche, ce matériau souffre de deux inconvénients majeurs pour cette application. Premièrement, le silicium ne présente pas une stabilité électrochimique suffisante (tendance à l'oxydation) pour maintenir les performances du dispositif sur la durée. Deuxièmement, l'inclusion de porosité dans le silicium abaisse considérablement sa conductivité électrique ce qui limite ses performances au cours de cycles de charge/décharge du composant. Pour pallier ce problème, nous proposons d'étudier le recouvrement du silicium poreux par une couche de nitrure de titane (TiN) qui aura à la fois le rôle de stabiliser chimiquement l'électrode et d'assurer une conduction efficace des charges électriques. La réalisation d'un dépôt conforme dans des structures présentant un degré de structuration similaire au silicium poreux est un défi technologique que peu de méthodes de dépôt peuvent relever. L'ALD (Atomic Layer Deposition) permet – dans des conditions optimisées – de recouvrir des structures aux pores nanométriques par un matériau comme le TiN. Dans le cas présent, l'objectif était le dépôt d'une couche de TiN de 2 nm environ recouvrant les parois latérales des pores. Des caractérisations MEB et EDX ont été réalisées pour confirmer l'uniformité du dépôt de la couche conductrice à l'intérieur de la porosité. Enfin, des caractérisations électrochimiques ont été effectuées pour déterminer les performances des micro-supercondensateurs ; des capacités de charge d'environ 500 µF/cm² ont été obtenues en milieu aqueux Na_2SO_4 1 M.

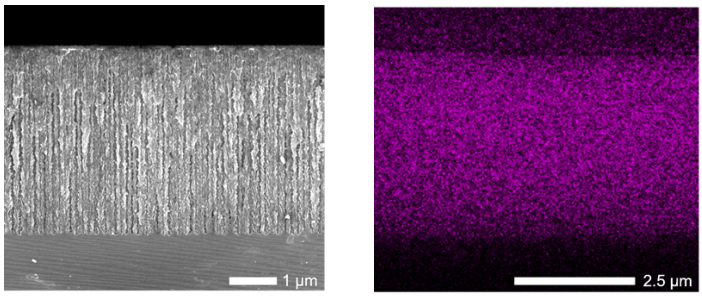

FIG. 1 –*Vue en coupe d'une couche de silicium poreux recouverte de TiN par ALD (à gauche). Signature élémentaire (EDX) du Ti dans la couche poreuse (à droite).*

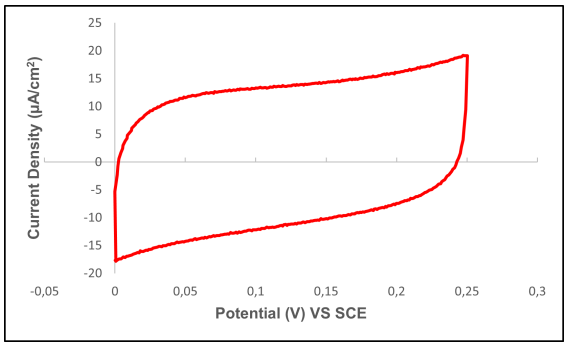

FIG. 2 – *Caractérisation électrochimique d'une électrode silicium poreux recouverte de TiN (ALD) par voltammétrie cyclique (vitesse de balayage 20 mV/s dans une solution aqueuse de Na_2SO_4 (1 M)).*

[1] Gautier, G., Billoué, J., Defforge, T., Menard, S. et Desplobain, S. (2019). *Intégration du silicium poreux dans les dispositifs micro-électroniques : avancées récentes,* Journées SCOPe 2019, 19-20 Juin. Paris.

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