GDR CNRS 3751 B2i
Bio-Ingénierie des Interfaces

11ème journée thématique

Techniques avancées de caractérisation de matière molle, biointerface ou biodispositif

12 octobre 2023

PARIS - Campus Pierre et Marie Curie

GDR Groupement de recherche B2i Bio-ingénierie des interfaces

Programme

9:25	**Accueil des Participants** **Installation des posters** **Mot d'accueil Vincent Humblot**
9:30	**Conférence invitée** **Laurent VONNA** (Mulhouse) : *Mouillabilité, techniques de base et avancées.*
10:15	O1- **Alberto MEZZETTI** (Paris) : *Rapid-scan & Step-scan FTIR spectroscopy in the Mid and Near Infrared applied to biosystems – from biointerfaces to living organisms -*
10 :35	O2- **Véronique Schoulpt** (DataPhysics Instruments GmbH, Metz) : *Characterising superhydrophilic dental implant surfaces Using imaginary water contact angles.*
10:55	**Conférence invitee** **Arnaud DELCORTE** (Louvain-la-Neuve, Belgium) : *New perspectives for soft matter analysis by SIMS.*
11 :40	O3- **Olivier HEINTZ** (Dijon) : *Développements récents des techniques XPS/HaXPES pour l'étude des biomatériaux.*
12:00	**Pause déjeuner & posters/tests appareils**
14:00	**Conférence invitée** **Marc SCHMUTZ** (Strasbourg) : *Cryo TEM et cryo SEM, quels apports pour l'étude de la structure de la matière molle.*
14:45	O4- **Frédéric GOBEAUX** (Gif-sur-Yvette) : *Combining SAXS-WAXS, SANS and cryoTEM to characterize nanodrugs structure and their interaction with proteins.*
15:05	O5- **Cloé DESMET** (Ispra, Italy) : *Hydrophobicity index, a newly harmonised method for nanomaterials characterisation.*
15:25	**Pause café & posters/tests appareils**
16:20	O6- **Nicolas BAIN** (Villeurbanne) : *Solid Marangoni Stresses and local TFM.*
16 :40	O7- **Dahlia SAAD** (Ecully) : *3D-AFM: A new technique for the characterization of solid/liquid interfaces.*
17 :00	**Mot de clôture - Fin de la journée**

Programme Posters

Development of a double layer electrospun patch for the treatment of myelomeningocele.
Khaoula BENABDDERRAHMANE , Salah RAMTANI , Julien STIRNEMANN , Céline FALENTIN-DAUDRE

AFM reveals the interaction and nanoscale effects imposed by squalamine on Staphylococcus epidermidis.
Sofiane EL-Kirat-Chatel, Mihayl Varbanov, Chloé Retourney, Elsa Salles, Arnaud Risler, Jean-Michel Brunel, Audrey Beaussart

TOF-SIMS et XPS pour l'étude de la fonctionnalisation de Nanobâtonnets d'or.
Olivier HEINTZ, Mélanie Romain , Wilfrid Boireau, Abdelmnim Radoua, Olivier Micheau, Nadine Millot

From Langmuir Blodgett to grafted films: towards the design of antibacterial titanium surfaces.
Jérôme Médard, Tan Sothéa-Ouk, Ronan Florennes, Christophe Piesse, Jean Pinson, Jean-Philippe Michel

Surface functionalization of non-woven polypropylene (PP) using plasma treatment: chemical and biological approaches to induce antimicrobial properties.
Tianyue WEI, Caroline AYMES-CHODUR, Christophe REGEARD, Nadine AUBRY-BARROCA, Philippe ROGER

Bioactive polymer grafting onto silicone breast implants surface to improve biological response.
Anna WOZNIAK, Vincent Humblot, Romain Vayron, Rémi Delille, Céline Falentin-Daudré

RÉSUMÉS COMMUNICATIONS ORALES

Conférence invitée

Wettability: basic and advanced techniques

Laurent VONNA*

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In this presentation, I will discuss the classical techniques for characterizing the wettability of solid surfaces, and in particular those based on the droplet and the Wilhelmy balance. The various methodologies and concepts on which these techniques are based will be reviewed. The discussion will be based on examples and possible artifacts specific to these techniques. Secondly, I will look at the wettability of rough or textured surfaces, showing how this physical property influences interaction with a liquid. By extension, the characterization of very low-wettable surfaces (superhydrophobic and superoleophobic) will be discussed. Finally, and following on from the wettability of textured surfaces, I will conclude with a presentation of Slippery Liquid-Infused Porous Surfaces (SLIPS).

Mots-Clés : mouillabilité, goutte posée, superhydrophobe, superoléophobe

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Rapid-scan & Step-scan FTIR spectroscopy in the Mid and Near Infrared applied to biosystems – from biointerfaces to living organisms

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Time-resolved FTIR spectroscopy (in the rapid and step-scan modes) is a very useful technique in the study of biochemical reactions, biointerfaces or even biodevices. It is also widely applied in other fields, such as catalysis, material science or photochemistry[(1,2)].

Whereas the technique has been used for more than 30 years, only recently it has become a widespread technique (used by hundreds of labs in the world) ; in some disciplines (e.g. molecular photobiology) this technique is nowadays considered not only a standard technique, but a mandatory one to caracterize a photoactive protein[(3)].

In this talk I will describe some results obtained in LRS laboratory using a recently-acquired FTIR spectrometer, whose utilization is also open (under some conditions) to any researcher.

First, it will be shown how the technique can be used to investigate biomolecules on inorganic surfaces[(4)] and their reactivity (temperature-induced and light-induced[(5)]).

Then, we will describe results obtained on living samples[(6)] and how the technique makes it possible to investigate the mechanism of biochemical reactions.

Finally, the relevance of experiments in the NIR[(7)] (particularly useful to characterize the influence of the hydration state of the sample) will also be described.

Références :

(1) A. Mezzetti, J. Schnee, A. Lapini, M. Di Donato Time-resolved infrared absorption spectroscopy applied to photoinduced reactions: how and why, Photochem Photobiol Sci 2022, 21, 557-584

(2) J.-M. Andansson, A. Baiker, Exploring catalytic solid/liquid interfaces by in situ attenuated total reflection infrared spectroscopy, Chem. Rev. 2010, **39**, 4571-4584

(3) A. Mezzetti, Photobiological reactions studied by time-resolved infrared spectroscopy, Photochemistry, Specialistic Periodical Report, 2020, 47, 159-195

(4) H Abadian, P Cornette, D Costa, A Mezzetti, C Gervais, JF Lambert, Langmuir, 2022, 38, 8038-8053.

(5) G. Sipka, M. Magyar, A. Mezzetti, P. Akhtar, Q. Zhu, Y. Xiao, G. Han, S. Santabarbara, J.-R. Shen, P. H Lambrev, G. Garab, Light-adapted charge-separated state of photosystem II: structural and functional dynamics of the closed reaction center, Plant Cell 2021, 33, 1286-1322

(6) M. Alexandre, A. Meezzetti, C. Buchel, B. Robert, in preparation

(7) M Malferrari, A Mezzetti, F Francia, G Venturoli BBA-Bioenergetics 2013, 1827, 328-339

Mots-Clés : vibrational spectroscopy, reaction mechanism, biomolecule-surface interactions, hydration state, in vivo monitoring of reactions.

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DataPhysics Instruments GmbH, société allemande forte de 25 ans d'expérience, est spécialisée dans la technologie de mesure pour la science des surfaces. La société propose une large gamme d'appareils permettant d'analyser les propriétés chimiques et physiques des surfaces et des interfaces, telles que la tension interfaciale, l'énergie de surface, le travail d'adhésion, les angles de contact statiques et dynamiques, les profils de rugosité, le potentiel zêta et la stabilité de dispersions et suspensions. En bref, nos produits permettent de déterminer les propriétés des matériaux lorsqu'un liquide rencontre un autre liquide ou une surface solide. Notre gamme comprend des mesureurs d'angle de contact (série OCA), des tensiomètres à force (série DCAT) et tensiomètres à goutte tournante (SVT25), des systèmes d'analyse de la stabilité de dispersions (MS20), des analyseurs de profil de surface (SPA 25) et des analyseurs de potentiel zêta (ZPA 20). Nous réalisons également des prestations de mesures sous contrat dans notre centre d'application.

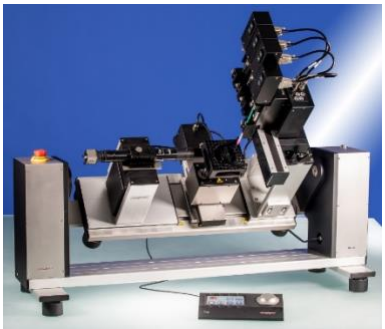
Analysing challenging surfaces at the example of dental implants

Measuring on Structured Test Areas

Une condition essentielle pour une mesure précise de l'angle de contact est que la goutte ne touche pas ou ne mouille pas au-delà du bord de la surface d'essai. Cela pose le défi de doser des gouttes particulièrement petites lors de l'analyse d'échantillons micro-structurés comme des implants, les cartes de circuits imprimés, les petits produits médicaux, les structures lithographiques, les composants de mécanique de précision et d'assemblage, les fils et les fibres uniques. Ce défi est relevé par le système de dosage picolitre innovant PDDS de DataPhysics Instruments. Le système de dosage de picolitres PDDS peut doser de manière reproductible des gouttelettes d'une taille inférieure à 30 picolitres.

Measuring on Extremely Wettable Surfaces

L'angle de contact avec l'eau est un paramètre important pour caractériser la mouillabilité d'un matériau et le classer comme hydrophile ou hydrophobe. Sur les matériaux très hydrophiles, l'eau s'étale complètement sur la surface et l'angle de contact atteint 0°. Si de telles surfaces très hydrophiles sont recherchées, comme dans le développement de matériaux biocompatibles, la question se pose de savoir s'il est possible de distinguer des matériaux qui possèdent tous un angle de contact avec l'eau de 0° ? Comment identifier parmi eux celui qui présente la meilleure hydrophilie ? La réponse est : cela devient possible avec des angles de contact dits imaginaires. À notre connaissance, les tensiomètres DCAT de DataPhysics Instruments sont les seuls systèmes de mesure qui intègrent dans leur logiciel une détermination fiable et reproductible de l'angle de contact imaginaire. L'application de la méthode sera présentée ci-après à l'exemple des implants dentaires.



Analysing your samples : the exposed configuration

Conférence invitée

New perspectives for soft matter analysis by SIMS

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This contribution reviews a number of aspects of soft matter and in particular biological sample characterization using secondary ion mass spectrometry, from small cluster ion beam analysis and high-resolution imaging of fragment and molecular ions to damage-less desorption and transfer of intact biomolecules using large gas cluster ion beams (GCIB). Three main subjects will be presented (i) The use of sputtered fragment ions for the determination of protein and antibody orientation on surfaces and even for direct "ballistic" protein sequencing[(1)]. (ii) Surface molecular imaging of engineered bio-objects (including collagen nanotubes and hydrogels) and real tissue cross sections (brain, endometrium and cornea), with the perspective of enhancing molecular ion sensitivity using *in situ* deposited MALDI matrices[(2)]. (iii) The potential of large intact molecule desorption and transfer by GCIB, including new approaches for molecular microanalysis[(3)] as well as biosurface and biofilm nano-fabrication[(4,5)]. In addition to the experiments, we will show how molecular dynamics simulations can provide access to the detailed microscopic view of the interactions needed for their understanding and their prediction[(6)].

Références :

(1) A. M. Kotowska, G. F. Trindade, P. M. Mendes, P. M. Williams, J. W. Aylott, A. G. Shard, M. R. Alexander, D. J. Scurr, Protein Identification by 3D OrbiSIMS to Facilitate in Situ Imaging and Depth Profiling. Nat. Commun. 2020, 11, 5832.

(2) T. Daphnis, B. Tomasetti, V. Delmez, K. Vanvarenberg, V. Préat, C. Thieffry, P. Henriet, C. Dupont-Gillain, A. Delcorte, Improvement of lipid detection in mouse brain and human uterine tissue sections using in situ matrix enhanced secondary ion mass spectrometry, J. Am. Chem. Soc. Mass Spectrom., 2023, 34, 2259-2268.

(3) B. Tomasetti, C. Lauzin, A. Delcorte, Enhancing Ion Signals and Improving Matrix Selection in Time-of-Flight Secondary Ion Mass Spectrometry with Microvolume Expansion Using Large Argon Clusters, Anal. Chem., 2023, 95, 13620-13628.

(4) V. Delmez, H. Degand, C. Poleunis, K. Moshkunov, M. Chundak, C. Dupont-Gillain, A. Delcorte, Deposition of Intact and Active Proteins In Vacuo Using Large Argon Cluster Ion Beams, J Phys Chem Lett. 2021, 12, 952–957.

(5) V. Delmez, B. Tomasetti, T. Daphnis, C. Poleunis, C. Lauzin, C. Dupont-Gillain, A. Delcorte, Gas Cluster Ion Beams as a Versatile Soft-Landing Tool for the Controlled Construction of Thin (Bio) Films, ACS Appl Bio Mater. 2022, 5, 3180–3192.

(6) S. Bertolini, A. Delcorte, Reactive molecular dynamics simulations of lysozyme desorption under Ar cluster impact, Appl. Surf. Sci. 2023, 631, 157487.

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Développements récents des techniques XPS/HaXPES pour l'étude des biomatériaux

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La spectroscopie de photoémission (XPS) consiste à mesurer l'énergie cinétique des électrons émis par un matériau à étudier sous l'effet d'un faisceau de rayons X monochromatique incident. C'est une technique d'analyse nécessitant la présence de l'utra-vide et elle est dite « de surface » puisque la profondeur d'information est systématiquement inférieure à 10 nm. En outre, l'XPS présente la particularité de permettre d'identifier l'environnement chimique de l'ensemble des éléments de la classification périodique à partir du lithium. La spectroscopie de photoémission est donc incontournable dès lors qu'il s'agit d'appréhender la nature des liaisons que mettent en jeu des éléments tels que le carbone, l'oxygène ou bien l'azote.
Le développement récent de sources de rayons X dures (par exemple la radiation $K_{\alpha 1}$ du chrome à 5414,8 eV) sur des machines de laboratoire permet d'étendre l'épaisseur analysée au-delà de 20 nm faisant de l'XPS une véritable technique d'analyse "volumique", à même de caractériser des échantillons dans leur globalité ainsi que la nature d'interfaces enfouies. Par ailleurs, cette approche a pour conséquence de diminuer drastiquement les artefacts de mesure liés à la présence systématique de carbone de pollution sur les échantillons et donc d'offrir des possibilités d'analyses plus fines pour des matériaux ou des échantillons organiques.
Au laboratoire ICB, de telles mesures sont aujourd'hui possibles à température cryogénique (Cryo XPS/HaXPES) de telle sorte que des échantillons biologiques ou hydratés peuvent également être introduits sous ultra-vide et analysés du point de vue de leur chimie.
Des exemples de telles analyses seront présentés, en particulier pour la fonctionnalisation de matériaux pour des applications médicales.

Références :

1. Kjaervik M.., et al., *Comparative Study of NAP-XPS and Cryo-XPS for the investigation of surface chemistry of the bacterial cell-envelope*. Frontiers in Chemistry 2021. **9 - 666161**.
2. Burrows, N.D., et al., *Surface Chemistry of Gold Nanorods.* Langmuir, 2016. **32**(39): p. 9905-9921.

Mots-Clés : CryoXPS, CryoHaXPES, Fonctionnalisation

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Conférence invitée

Cryo TEM et cryo SEM, quels apports pour l'étude de la structure de la matière molle.

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Combining SAXS-WAXS, SANS and cryoTEM to characterize nanodrugs structure and their interaction with proteins

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Since their inception, the integration of nanotechnologies in the biomedical domain has borne many promises, notably in terms of drug vectorization. Indeed, formulating active ingredients under the form of nanoparticles enables to increase their efficacy (with a high bioavailability) while reducing their toxicity, to combine different modes of action and to control their targeting and release in the body. However, beyond the therapeutic efficacy of the nanodrugs, controlling their structure, colloidal stability and fate in the body is crucial to ensure the safety of the patients. Also, despite the researchers' enthusiasm to design innovating nanodrugs, only a few have actually reached the market. Indeed, not only the translation to industrial scale may be complex but the *in vivo* behaviour of nanoparticles is hard to predict. Moreover, *in vivo* studies are costly and complex, and do not always enable to fully understand the molecular interactions at play. A thorough physico-chemical characterization of these systems is thus crucial to be able to use them in complete confidence.

In collaboration with researchers from Galien Institute and INSERM (Hôpital Kremlin-Bicêtre), we have developped a methodology to study suspensions of prodrug nanoassemblies. These prodrugs result from the bioconjugation of an active principle (nucleosides, peptides, siRNA) with squalene, a biosourced lipid that drives the supramolecular assemblies. Through several examples, we will show the contribution of radiation scattering (neutrons and x-ray) and cryoTEM to the assessment of the structure and colloidal stability of these nanoassemblies.[1,2] We will also show how these tools, along with spectroscopies, provide a wealth of information to describe the interactions between these nanodrugs and different components of biological medium (full sera, albumin, haemoglobin and lipoproteins).[2-5] These studies allowed us to analyse the different kinds of interactions at play, whether considering the monomeric prodrugs, the nano-assemblies or the proteins. We have thus demonstrated that serum albumin is able to disassemble nano-assemblies by extracting the monomeric prodrug to form complexes. This mechanism appears to be generic for all the squalene-based prodrugs. Albumin would thus contribute to prodrug transport in the bloodstream and the nanoassemblies could be seen as circulating prodrug reservoirs.

Références :

[1] Dormont et al. (2019) *Journal of Controlled Release* 307 302-314.
[2] Caillaud et al. (2021) *International Journal of Pharmaceutics*
[3] Gobeaux et al. (2020) *Nanoscale* 12 2793-280910.
[4] Lepêtre et al. *under review*
[5] Gobeaux et al. *in preparation*

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Mots-Clés : soft nano-assemblies, nanodrugs, proteins,

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Hydrophobicity index, a newly harmonised method for nanomaterials characterisation

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Hydrophobicity represents the tendency of a substance to repel water. It is an important physico-chemical property that may influence the fate of nanomaterials in the environment and biological matrices. However, there was a methodological gap since existing standardised methods were not suitable for nanomaterials (NMs). A new method to determine the "Hydrophobicity index" of nanomaterials was developed, based on the measurement of the affinity of NMs to engineered hydrophobic and hydrophilic surfaces called collectors [1,2].
Particles in dispersion are injected on the collectors and their binding is recorded in real time by Dark-Field microscopy. The number of bound particles as a function of time determines their affinity to the collector, which is directly influenced by the energy barrier occurring between the particles and the surface according to the XDLVO theory[3]. These measurements are used for the calculation of the Hydrophobicity index: $Hy = \log(v_{hy} / v_{max})$. The binding rate on the hydrophobic collector, v_{hy}, is directly related to the hydrophobicity of the particles. v_{max} is measured on the collector with opposite charge compared to the particles, where the binding rate is maximum due to the preponderant electrostatic attractive interactions. This index is a direct measurement of the tendency of the NM to bind to a hydrophobic surface.
The transferability of the method was evaluated through an inter-laboratory comparison study[4]. The variability of the measurements and the reproducibility of the calculation of the Hydrophobicity index were considered satisfactory according to the International Standard ISO 5725-2. The method was adopted by the OECD and published as Test Guideline 126[5].

References :

[1] Desmet C, Valsesia A, Oddo A, Ceccone G, Spampinato V, Rossi F, Colpo P. 2017. Characterisation of nanomaterial hydrophobicity using engineered surfaces. J Nanopart Res 19: 117.

[2] Valsesia A, Desmet C, Ojea-Jiménez I, Oddo A, Capomaccio R, Rossi F, Colpo P. 2018. Direct quantification of nanoparticle surface hydrophobicity. Commun Chem 1:53.

[3] Donaldson SH, Røyne A, Kristiansen K, Rapp MV, Das S, Gebbie MA, Lee DW, Stock P, Valtiner M, Israelachvili J. 2015. Developing a general interaction potential for hydrophobic and hydrophilic interactions. Langmuir 31 (7):2051-64.

[4] Desmet C, Roncari F, Gottardo S, Ponti J, Riego Sintes J, Colpo P, Valsesia A. 2023. Inter-laboratory comparison on the determination of the hydrophobicity index of nanomaterials through an affinity measurement. Publications Office of the European Union, Luxembourg, JRC133937.

[5] OECD. 2023. Test No. 126: Determination of the Hydrophobicity Index of Nanomaterials Through an Affinity Measurement, OECD Guidelines for the Testing of Chemicals, Section 1, OECD Publishing, Paris.

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Solid Marangoni Stresses and local TFM

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Despite its importance in any adhesion and wetting phenomena, there is a fundamental property that is not yet understood in soft solids: surface elasticity. Also called the Shuttleworth effect, surface elasticity is intimately linked to the solid physico-chemistry and can be boiled down to one question. Does stretching the surface of a soft solid change its surface tension? In 2021, we demonstrated that the mechanical response of a textured silicone gel could only be explained by an elastic surface(1). It is, however, still unclear whether the measured surface elasticity is a true material property or a mere consequence of the surface preparation. This presentation will focus on a novel experimental setup that exploits Marangoni stresses and local TFM techniques to characterize the surface mechanics of pristine surfaces.

Références :

(1) Nicolas Bain, Anand Jagota, Katrina Smith-Mannschott, Stefanie Heyden, Robert W. Style, and Eric R. Dufresne, Phys. Rev. Lett. 127, 208001 – Published 8 November 2021.

Mots-Clés : Soft solid, surface tension, TFM

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3D-AFM: A new technique for the characterization of solid/liquid interfaces

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Self-assembled or grafted onto organic monolayer on the solid surfaces of a solid-liquid interface can have the role of a sensing layer in biosensors, a protective layer in tribology processes or lab-on-chip systems. Therefore, studying the organization and the behavior of these layers in different environments is very important in order to further understand the application in which they are used. The purpose of our study is the characterization of these interfaces at the nanoscale by 3D-AFM, a newly developed technique for interfacial characterization[(1,2)]. AFM is used for surface characterization where a 2D topographical image of the surface is generated, and also as force spectroscopy where point-by-point (1D) force vs z-distance curves are measured. 3D-AFM is a combination between these two techniques where a 3D image of the phenomena occurring above the surface, i.e. the interface, is generated. In particular, we are interested in gold-thiol layer-liquid interfaces for biosensing and tribological applications. In this work, a 3D-AFM system is implemented in a conventional 2D-AFM apparatus (Park System's NX10). Four samples were used: pure gold, pure Poly(Acrylic Acid) PAA, pure Poly(Ethylene Glycol) PEG, and 50/50 PAA/PEO. We measured these samples in pure water and in a 0.01M PBS solution. The shifts in the frequency Δf recorded during the 3D-AFM scan were used in a Python program to create a 2D (xz) color coded cross-sectional image of the scanned samples. Our first experiments tend to show that this 3D-AFM method is appropriate to visualize the differences in behavior between the samples caused by different polymer chain-tip interactions during the measurement.

Références :

(1) T. Fukuma, R. Garcia, Atomic- and Molecular-Resolution Mapping of Solid–Liquid Interfaces by 3D Atomic Force Microscopy, ACS Nano, 2018, 12, 11785-11797.

(2) H. Asakawa, S. Yoshioka, K. Nishimura, T. Fukuma, Spatial Distribution of Lipid Headgroups and Water Molecules at Membrane/Water Interfaces Visualized by Three-Dimensional Scanning Force Microscopy, ACS Nano, 2012, 6, 9013-9020.

Mots-Clés : 3D-AFM, force spectroscopy, organic monolayer, polymer brushes

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cnrs GDR Groupement de recherche B2i Bio-ingénierie des interfaces

RÉSUMÉS POSTERS

Development of a double layer electrospun patch for the treatment of myelomeningocele

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Myelomeningocele (MMC) is a congenital malformation caused by a primary defect in neural tube closure during the embryological period. It is characterized by protrusion of the meninges and spinal cord through the open vertebral arches causing cognitive and motor dysfonctions. Fetal surgical repair has been shown to reduce cognitive symptoms but remains late for a better motor outcome, so an earlier foetoscopic repair would be preferable to reduce motor neurological symptoms and fetomaternal risks, by covering the defect with a patch intended to protect the exposed neural tissue. Previous work by the LBPS team allowed to develop a highly effective bioactive Polycaprolactone membrane, with excellent mechanical and biological properties. Based on this work, the aim of this study is to develop a biodegradable and waterproof bilayer patch, designed to cover and protect the spinal cord exposed in utero, with a bioactive side, suitable for cell proliferation, and an anti-adhesive side to avoid its attachment to the spine.

Mots-Clés : Myelomeningocele; PCL; Electrospinning; Bioactive polymer.

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AFM reveals the interaction and nanoscale effects imposed by squalamine on *Staphylococcus epidermidis*

Sofiane EL-Kirat-Chatel[1,2 *], Mihayl Varbanov[3], Chloé Retourney[1], Elsa Salles[1], Arnaud Risler[3], Jean-Michel Brunel[4], Audrey Beaussart[5,2]

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The Gram-positive bacterium *Staphylococcus epidermidis* is responsible for important nosocomial infections. With the continuous emergence of antibiotic-resistant strains, the search for new treatments has been amplified in the last decades. A potential candidate against multidrug-resistant bacteria is squalamine, a natural aminosterol discovered in dogfish sharks. Despite its broad-spectrum efficiency, little is known about squalamine mode of action.(1) Here, we used atomic force microscopy (AFM) imaging to decipher the effect of squalamine on *S. epidermidis* morphology, revealing the peptidoglycan structure at the bacterial surface after the drug action. Single-molecule force spectroscopy with squalamine-decorated tips shows that squalamine binds to the cell surface via the spermidine motif. A deeper analysis of the AFM force-distance signatures suggests the implication of the accumulation-associated protein (Aap), one of the main adhesins of *S. epidermidis*, in the initial binding of squalamine to the bacterial cell wall. This work highlights that AFM -combined with microbiological assays at the bacterial suspension scale- is a valuable approach to better understand the molecular mechanisms behind the efficiency of squalamine antibacterial activity. (2)

Références :
(1) Mammari *et al.* Microorganisms, 2022. DOI: 10.3390/microorganisms10061205
(2) El-Kirat-Chatel *et al.* Colloids Surf B Biointerfaces, 2023. DOI: 10.1016/j.colsurfb.2023.113324

Mots-Clés : *Staphylococcus epidermidis*, Squalamine, Atomic force microscopy, Antimicrobial, Aminosterol

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TOF-SIMS et XPS pour l'étude de la fonctionnalisation de Nanobâtonnets d'or

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Les nanobâtonnets d'or (AuNRs) sont apparus comme un matériau innovant qui suscite de grands espoirs en nanomédecine, notamment pour l'imagerie et la thérapie du cancer. En effet, les AuNRs présentent des propriétés optiques uniques qui découlent, grâce à leur anisotropie, de leurs résonances plasmoniques de surface longitudinales et transversales. Ils sont également biocompatibles et ont de remarquables capacités d'absorption et de diffusion de la lumière en proche infrarouge ce qui les rends particulièrement intéressants pour l'imagerie et la thérapie des cancers. Ils peuvent être produits de différentes manières, mais la synthèse de AuNRs assistée par l'argent à l'aide de germes d'or (seeds) est la méthode la plus développée et la plus adaptable à ce jour. Les AuNRs y sont produits par la réduction de l'acide chloroaurique par un agent réducteur faible (par exemple, l'acide ascorbique) en présence de bromure de cétyltriméthyl-ammonium comme agents directeurs et de traces de nitrate d'argent [1]. Il est généralement admis que le CTAB est présent à la surface des AuNRs terminés sous la forme d'une bicouche, par le biais d'interactions électrostatiques entre le groupe de tête ammonium et une surface anionique d'AuNRs constituée de complexes de bromure de métal [2].

Pour les applications biomédicales, il est nécessaire de fonctionnaliser la surface des AuNRs avec des molécules qui apportent stabilité, activité et surtout biocompatibilité. C'est pourquoi il est très important de bien étudier les couches de molécules en surface des nanostructures pour mieux comprendre leur comportement et réactivité.

Diverses techniques d'analyses peuvent apporter des réponses, comme la spectrométrie de photoélectrons X (XPS) ou la spectrométrie de masse d'ions secondaires à temps de vol (TOF-SIMS). Dans ces travaux, les analyses élémentaires XPS permettent de montrer, en comparant des échantillons préparés à diverses concentrations, que les couches de CTAB autour des nanobâtonnets sont bel et bien orientées. Les analyses permettent ensuite de vérifier, après fonctionnalisation, si le CTAB est éliminé et si le nouveau ligand est bien greffé.

Références :

1. Kozek, K.A., et al., *Large-Scale Synthesis of Gold Nanorods through Continuous Secondary Growth.* Chemistry of Materials, 2013. **25**(22): p. 4537-4544.
2. Burrows, N.D., et al., *Surface Chemistry of Gold Nanorods.* Langmuir, 2016. **32**(39): p. 9905-9921.

Mots-Clés : XPS, TOF-SIMS, Fonctionnalisation, AuNRS

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From Langmuir Blodgett to grafted films: towards the design of antibacterial titanium surfaces

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Several methods are available for the functionalization of metallic surfaces with organic films: Langmuir films, thiols on gold, silanes and phosphonic acids on oxidized surfaces, electroreduction of diazonium salts on metal oxidized or not, electrooxidation of amines and alcohols on carbon, Pt and Au. These different methods can be classified according to the strength of their attachment to the surface but also according to whether they provide organized or disorganized films. At one end of the classification, Langmuir-Blodgett films are only adsorbed, that is they are weakly attached, to the surfaces on which they are transferred but are solid crystalline monolayer films. At the other end one finds electrografted films that provide strongly bonded multilayered disordered films. This work presents a new method allowing the formation of a compact crystalline monolayer film strongly attached to a metallic surface was obtained by transfer of a Langmuir Blodgett film of octadecylamine to an Au or HOPG surface and simultaneous oxidative electrografting of this film still in contact with the aqueous subphase. Our most recent works describes the Langmuir Blodgett electroGrafting process surface reaction[1,2] applied to the functionalization of bulk titanium with Magainin 2 monolayer and the antibacterial effect of such modified surfaces.

Références :

M. Gabaji, J. Médard, A. Hemmerle, J. Pinson, J. P. Michel. From Langmuir−Blodgett to Grafted Films. Langmuir 2020, 36, 2534−2542.

[2] Jérôme Médard, Xiaonan Sun, Jean Pinson, Da Li, Claire Mangeney, Jean-Philippe Michel. Electrografting and Langmuir−Blodgett: Covalently Bound. Nanometer-Thick Ordered Films on Graphite. Langmuir 2021, 37, 12539−12547.

Mots-Clés : surface functionalization, Langmuir-Blodgett, electrografting, magainin 2, titanium.

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Surface functionalization of non-woven polypropylene (PP) using plasma treatment: chemical and biological approaches to induce antimicrobial properties.

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Because of the rapid spread of infectious disease, polypropylene (PP) medical-surgical masks have been produced on a very large scale, and this pandemic period has evidenced the need for new medical and health products. We aim to use the plasma treatment technology to induce the functionalization of the PP surface with antimicrobial components. Essential oils, which are potential bio sourced candidates, are intended to be grafted on the PP surface to fight against bacterial infections, by either restricting the growth of bacteria (bacteriostatic effect) or killing bacterial cells (bactericidal effect) (1). Essential oils are also an alternative to the use of classical antibiotics for which the emergence of resistance is increasing (2).
The results presented here show how we modified the molecules, intended to be grafted on the activated surface. With the background of the SM2ViE team (3), the chosen essential oils are chemically modified so that they are more prone to react with the target surface. In this study, we chose citronellol and geraniol compounds, known for their antimicrobial activity, and we used a chemo enzymatic hydrolysis with the help of lipase catalysis to transform the vinyl bonds into peroxide ones (4). Three bacterial species have been used: *Escherichia coli,* possessing two membranes (Gram-negative), *Staphylococcus aureus* with only one membrane (Gram- positive), and *Corynebacterium glutamicum* which possesses features of both Gram-positive and Gram-negative bacteria. After estimating the MIC (Minimum Inhibitory Concentration) and the MBC (Minimum Bactericidal Concentration) by turbidimetry test of citronellol and geraniol before and after modification, further tests were conducted (bacteria growth curves, killing analysis, zeta potential, contact angle, SEM). Through a comparative analysis of zeta potential data and SEM, we discovered that the selected terpenes caused significant damage to the bacterial membrane of *Escherichia coli* at a specific concentration. However, these terpenes did not appear to have a discernible impact on the membranes of the other two bacterial species. Additionally, we conducted contact angle tests to investigate these bacteria' hydrophilic and hydrophobic properties.

References:

(1) S. Tariq et al., A comprehensive review of the antibacterial, antifungal and antiviral potential of essential oils and their chemical constituents against drug-resistant microbial pathogens, 2019.
(2) M.E.A. de Kraker, et al., Will 10 Million People Die a Year due to Antimicrobial Resistance by 2050, 2016.
(3) H. Salmi-Mani et al., Poly (ethylene terephthalate) films modified by UV-induced surface graft polymerization of vanillin derived monomer for antibacterial activity, 2018.
(4) E.G. Ankudey, et al., Lipase-mediated epoxidation utilizing urea–hydrogen peroxide in ethyl acetate, Green Chem,2006.

Keywords: Biocompatible polymers, Antimicrobial and antifouling properties, Surface functionalization, Plasma grafting, Physicochemical analysis.

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Bioactive polymer grafting onto silicone breast implants surface to improve biological response

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Poly(dimethyl siloxane) (PDMS) is one of the most widely used material in the biomedical field. Despite its numerous advantages, its hydrophobic character promotes bacterial adhesion and biofilm formation. For breast implants, the biocompatibility is challenged due to the biofilm formed around the implant that can degenerate to severe capsular contracture over time(1). The LBPS team has set up a strategy to prevent bacterial contamination and capsular contracture formation by covalently immobilizing hydrophilic biopolymers on the surface of the implant. The technic involves a pre-irradiation (UV) step which generates radical sites allowing a "grafting from" polymerization step. The team has already worked on the grafting of an anionic biopolymer: the poly(styrene sodium sulfonate) on silicone surface in order to improve its biocompatibility(2). However, it was no sufficient to prevent bacteria adhesion. Now the work focuses on the impact of grafting carboxylate groups carried by biopolymers. Polyacrylic acid (PAA) as a non-toxic and biocompatible biopolymer seems to be a great candidate to bring antiadhesive property to repel bacteria or a bactericidal property to kill adhered bacteria(3). X-Ray Photolectron Spectroscopy (XPS) and FTIR analysis have demonstrated the covalent grafting of this polymer. Water contact angle measurements have highlighted the change in hydrophilicity on the surface, and a colorimetric assay allowed us to assess the grafting rate of PAA. Tensile strength assays were performed to ensure that the functionalization process does not significantly alter the material's mechanical properties.

Références :

(1) M. Lam, V. Migonney, C. Falentin-Daudre, *Acta Biomateriala*, **2021,** *121*, 68-88.

(2) M. Lam, V. Moris, V. Humblot, V. Migonney, C. Falentin-Daudré, *European Polymer Journal*, **2020,** *128*, 109608

(3) H. Arkaban, M. Barani, M. Akbarizadeh, N. Chauhan, S. Jadoun, M. Soltani, P. Zarrintaj, *Polymers*, **2022,** *4*(6), 1259.

Mots-Clés : Silicone, Grafting, Biomaterial, Surface functionalization.

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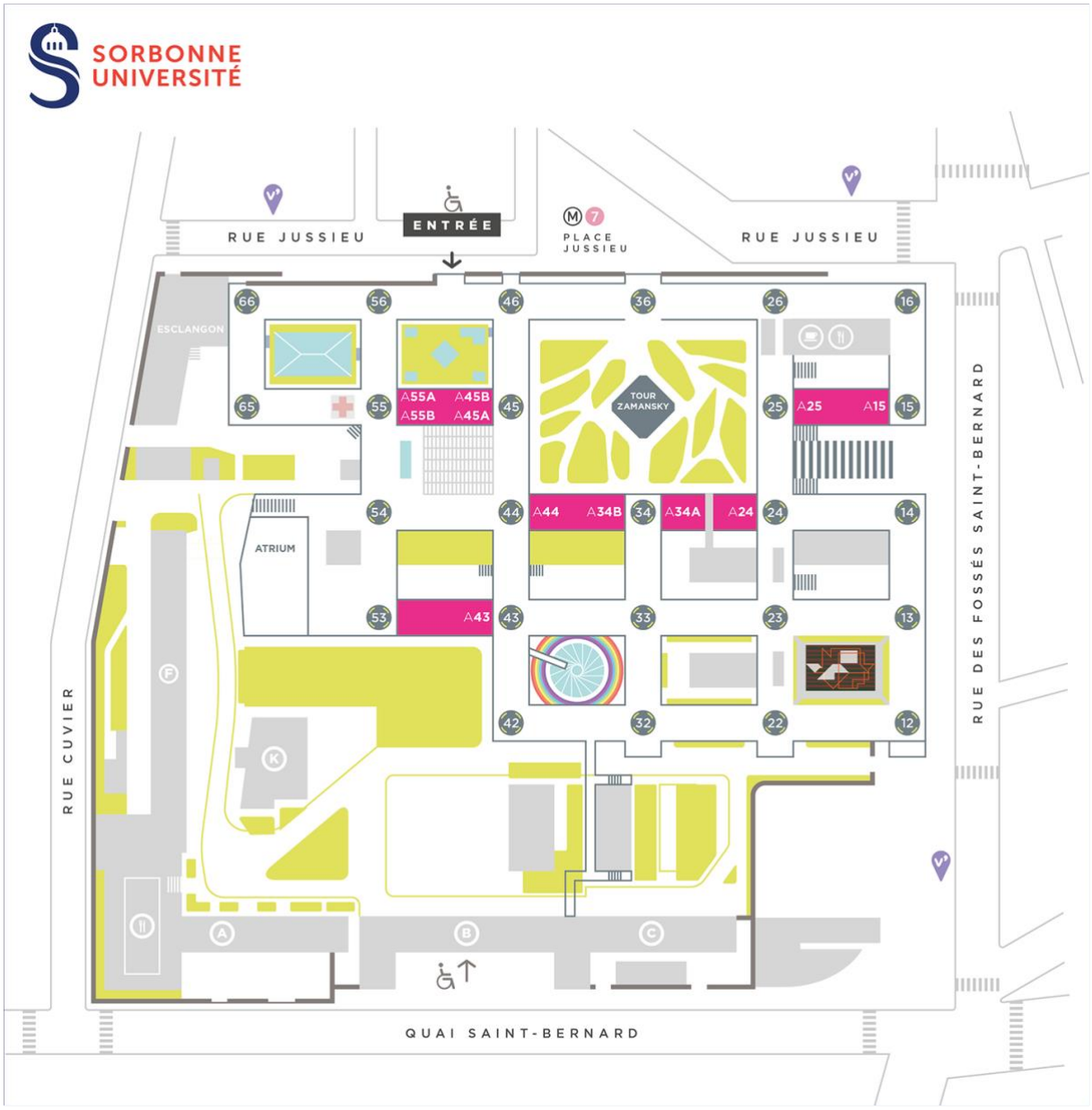

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