Surface Modification for Chemical and Biochemical Sensing SMCBS 2023

IChF Institute of Physical Chemistry PAS

11th International Workshop on Surface Modification for Chemical and Biochemical Sensing

Program and the Book of Abstracts

Łochów, Warsaw, Poland
3–7 November 2023

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Łochów – discover the unknown

The facade of the Palace in Łochów

Although Łochów is a small town, it carries a huge dose of Polish history. We can reflect on it by looking at the Palace in Łochów, preserved to this day – a property dating back to the 1830s, built in the neo-Gothic style, logistically important due to its tactical location near the Paris-Petersburg railway line, which was then under construction.

The stunning interior, decorated in the neo-Gothic style typical of the 19th century, is an inseparable element of the Palace. This allows us to go back in time and feel the magic of the Podlasie village of that time. Palace furniture decorations combined with wooden floor finishes create perfect harmony, giving the Palace a unique atmosphere.

Interiors of the Palace in Łochów

The Island of Poets and Writers in Łochów

When citing history, we cannot omit the famous Polish poet Cyprian Kamil Norwid (1821–1883), closely associated with Łochów. Norwid spent his youth in the palace and its surroundings, creating works that are still analyzed today. In order to commemorate Łochów's connection with poetry, there are currently twelve wooden sculptures of famous Polish writers, including Norwid (photo on the left), which we can admire while walking around the Park and Palace Complex.

Warsaw – the capital bustling with life

Baroque-classicist royal castle, rebuilt after complete destruction during World War II. Together with the Old Town, it is included on the UNESCO World Heritage List. The Constitution of 3 May 1791, considered the first in Europe and the second in the world, was signed in this Castle. Moreover, it was the meeting place of the Sejm and the residence of the President of the Republic of Poland. Currently, it serves as a museum and representative building.

Royal Castle in Warsaw

Warsaw city skyline

The modern center of Warsaw impresses with its soaring buildings, including the Palace of Culture and Science, characteristic of the city skyline. The city center, easily approachable by a well-organized public transport network, offers tourists many entertainment venues, museums and theaters, as well as parks. The bustling center looks especially beautiful at night, sparkling with various colors.

An integral part of coming to Warsaw is a walk around the Old Town. Colorful tenement houses and charming, narrow streets surrounding the Royal Castle attract the attention of visitors. The very center of the old town is guarded by another monument of the Warsaw Mermaid. It is also a great place to try Polish cuisine, especially the famous pierogi and traditional soups.

Warsaw Old Town

Warsaw Royal Route from the observation deck

Just behind the castle begins Wasaw Royal Route, a historical route leading from the Royal Castle to the Palace of King Jan III Sobieski in Wilanów. The most representative part of the route are Krakowskie Przedmieście street with the Presidential Palace, Nowy Świat and Aleje Ujazdowskie. A wonderful view of the Route and the city skyline can be observed from the observation deck opposite the Royal Castle.

Discover Warsaw at night! In the summer season, shows of the Multimedia Fountain Park take place near the Royal Castle. It is the second largest multimedia fountain in Poland, which attracts tourists visiting Warsaw and residents in the evenings. The main point of the park is a multimedia fountain, the water of which creates a 10 m high wall and can be used to show films and arrange laser shows.

Multimedia Fountain Park in Warsaw

Warsaw Mermaid

The mermaid – half woman, half fish – is the heroine of several Warsaw legends, and is currently part of Warsaw coat of arms. According to legend, she served as the patron and protector of the city. The most popular representation of the Mermaid is the monument located right next to the Vistula River (in the photo on the left), which was prepared before the outbreak of World War II. Currently, it is a popular tourist attraction, interesting for those walking along the Vistula Boulevards.

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ISBN: 978-83-939295-5-9

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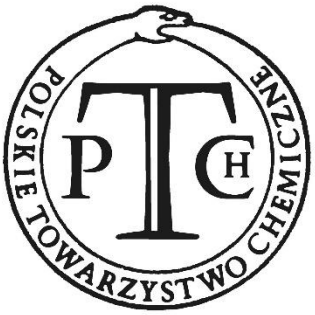

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Welcome address

On behalf of the Organizing Committee and Scientific Advisory Board, we are delighted and honored to welcome you all. With great pleasure, we present you the Program and Abstracts of the 11th International Workshop on Surface Modification for Chemical and Biochemical Sensing, SMCBS 2023. The Workshop is organized by the Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw (Poland). This Workshop received financial support from the state budget funds granted by the Polish Minister of Education and Science within the "Excellent Science II" program.

Previous SMCBS workshops were organized in Białowieża (2003), Kazimierz Dolny (2005), Włodowice (2007), Przegorzały near Cracow (2009), Łochów (2011 & 2013), Pułtusk (2015), and Żelechów (2017 & 2019). Because of the COVID-19 pandemic, the 10th Workshop was hosted online. Since starting, this Workshop has provided a platform for sharing and exchanging views between experienced scientists and young researchers. Similarly, as formerly, the present interdisciplinary Workshop involves the science of chemical and non-chemical modification of solid surfaces. The SMCBS Workshop program contains different sensing aspects, biomaterials for catalysis, and energy-generating devices. So, a broad spectrum of participants will enjoy this interdisciplinary meeting. Moreover, synthetic receptors-based recognition system designing and its application in chemosensing are included because of broad interest and constant growth in the field. Topics covered by presentations at the SMCBS 2023 Workshop involve but are not limited to:

- chemo- and biosensing
- chemical and biochemical surface modification
- polymer film coating
- inorganic, organic, and biomaterials for catalysis as well as for electric energy generation and storage
- charge transport in surface films
- novel techniques and instrumentation for surface examination
- signal transduction and processing, detection techniques and protocols, system miniaturization, and nanotechnology use

We are pleased that scientists of international recognition have accepted our invitation to deliver tutorial lectures. We thank specialists in their fields for sharing their latest breakthrough results presented as keynote lectures. We are happy to welcome young scientists who will present their results as short oral communications or posters. We expect fruitful and constructive discussions during all sessions.

The Organizing and Program Committee sincerely thank all those who helped to make the 11th SMCBS 2023 Workshop possible. We are particularly thankful to the International Scientific Advisory Board members for their outstanding job in suggesting keynote speakers suitable for the scientific profile of the event. We also thank the Authors and session chairing persons for their valuable contribution to making this event possible. We wish you all a wonderful time at the Workshop, both scientifically and socially.

Welcome to Warsaw!

On behalf of the Organizing and Program Committee of the 11th SMCBS 2023 Workshop

Piyush Sindhu Sharma

Chair

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The Workshop is organized by the Institute of Physical Chemistry of the Polish Academy of Sciences.

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The project is partially financed by state budget funds granted by the Polish Minister of Education and Science within the "Excellent Science II" program.

SMCBS 2023 from all over the world

This year, the walls of Łochów Palace and Manor Farm are hosting distinguished guests from as many as 21 countries on 4 continents. We warmly welcome representatives affiliated with:

- Austria,
- Brazil,
- Bulgaria,
- Canada,
- Croatia,
- Czech Republic,
- Denmark,
- Estonia,
- Finland,
- France,
- Germany,
- Hungary,
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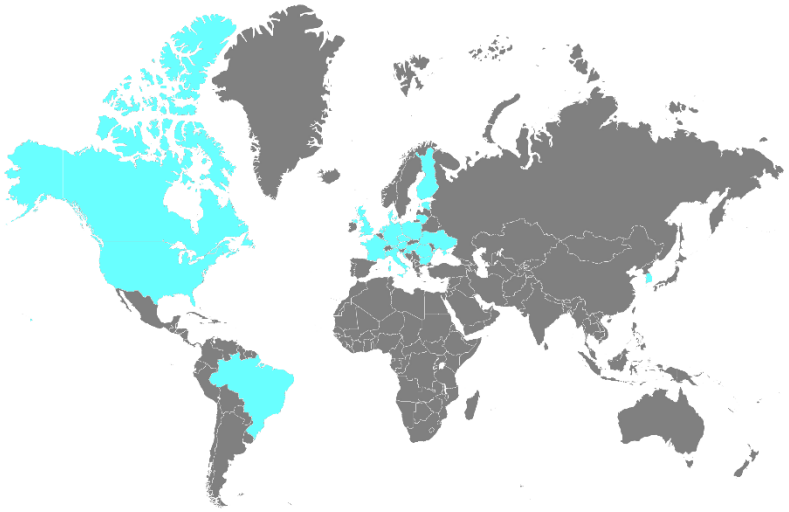

The 20-year tradition of the SMCBS Workshops has already brought fame worldwide. We feel honored to co-create this tradition, gathering in such a large group. We hope that the 11th edition of the International Workshop on Surface Modification for Chemical and Biochemical Sensing will be an unforgettable experience, rich in new memories, meeting new people, and sharing a common passion, just like in the past years.

SMCBS 2023

11th International Workshop on Surface Modification for Chemical and Biochemical Sensing

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Organized by the Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland

Łochów, Warsaw, Poland
3–7 November 2023

SMCBS 2023 Program

Friday, November 3

09:00–17:00		**Registration at the IPC PAS**
11:30–16:30		**Lunch at a nearby restaurant**
13:30		**Departure of the 1st bus to Łochów**
17:00		**Departure of the 2nd bus to Łochów**
16:00–19:00		**Setting up posters in the Venue**
19:00–20:00		**Dinner**
20:00–21:20		**Evening session** Chairs: A. Giannetti / F. Lisdat
20:00–20:45	T01	**Renata Bilewicz** Gold Clusters Doping Lipid Layer Act as Remote Nanoelectrodes towards Electroactive Probes
20:45–21:05	K01	**Frank Marken** Coupling Ionic Diodes in Membranes for Desalination and Electroosmotic Water Transport
21:05–21:20	SC01	**Magdalena Wiloch** Spectroelectrochemical Studies of a Potential Drug Against Alzheimer's Disease

Saturday, November 4

08:00–09:00		**Breakfast**
09:00–10:40		**Morning session 1** Chairs: V. Ostatná / W. Nogala
09:00–09:45	T02	**Alexander Kuhn** Bipolar Nanoelectrochemistry for Controlled Surface Modification
09:45–10:05	K02	**Serena Arnaboldi** Electromechanical Systems for the Enantioselective Wireless Loading and Release of Fluids
10:05–10:25	K03	**Fred Lisdat** Recent Progress in Coupling Photoactive Protein Complexes to Electrodes
10:25–10:40	SC02	**Mario Mitov** Simultaneous Gold and Silver Recovery in Microbial Fuel Cells Operating in a Short-Circuited Mode

10:40–11:10		**Coffee break**
11:10–13:05		**Morning session 2** Chairs: A. Canciu / J. Ryl
11:10–11:30	K04	**Larysa Baraban** Nanoelectronics for Cancer Therapy
11:30–11:50	K05	**Elena Ferapontova** Interfacial Design of Electrocatalytic DNA- and Aptasensors
11:50–12:10	K06	**Mathieu Etienne** Nicotinamide Cofactor – Dihydrogen Interconversion for Electrosynthesis
12:10–12:30	K07	**Svyatoslav Kondrat** The Role of Quantum Capacitance in Capacitive Energy Storage with Low-Dimensional Electrodes
12:30–12:50	K08	**Liang Liu** Scanning Gel Electrochemical Microscopy for Surfaces Examination and Modification towards Biological Applications
12:50–13:05	SC03	**Adrian Olejnik** Structure and Photoelectrochemistry of the Laser-Graphitized Polydopamine Coating
13:15–14:45		**Lunch**
14:45–16:20		**Afternoon session 1** Chairs: E. Ferapontova / P. Pięta
14:45–15:05	K09	**Chloé Grazon** From Quantum Dots to Fluorescent Organic Nanoparticles: Bright Nanotools for Biosensing
15:05–15:25	K10	**Andreas Lesch** Print-Light-Synthesis for Large-Scale Fabrication of Metal Films for Electrochemical Sensing
15:25–15:45	K11	**Insung Choi** Single-Cell Nanoencapsulation: Past, Present, and Future
15:45–16:05	K12	**Ambra Giannetti** Signal-Off SERS Biosensor Based on a Molecular Beacon for miRNA Detection
16:05–16:20	SC04	**Maria Madej** Voltammetric Biosensor Based on Horseradish Peroxidase and MOF JUK-2 for 17-β-Estradiol Determination
16:30–17:00		**Coffee break**
17:00–19:00		**Poster session**
19:00–20:00		**Dinner**

Sunday, November 5

08:00–09:00		**Breakfast**
09:00–10:40		**Morning session 1** Chairs: C. Branger / M. Cieplak
09:00–09:45	T03	**Karsten Haupt** Synthetic Peptide Antibodies – Principle and Application of Molecularly Imprinted Polymer Nanogels Specific for Protein Epitopes
09:45–10:05	K13	**Peter Lieberzeit** A Closer Look to the Interface: Factors Governing Binding Between Molecularly Imprinted Polymer Thin Films and Their Targets
10:05–10:25	K14	**Petar Kassal** Inkjet Printing of Electrodes for Flexible Electrochemical Sensors
10:25–10:40	SC05	**Alessia Di Fiore** Synthesis and Surface Coating of Molecularly Imprinted Polymer Nanogels Specific for the Heart Failure Biomarker Troponin T
10:40–11:10		**Coffee break**
11:10–13:15		**Morning session 2** Chairs: J. Maciejewska-Komorowska / G. Blanchard
11:10–11:55	T04	**Paweł Kulesza** Low-Temperature Reduction of Electrochemically Inert Molecules: Oxygen, Carbon Dioxide and Nitrogen
11:55–12:15	K15	**Paolo Bollella** Smart Enzyme Conductive Inks for Enzyme-Based Amperometric Biosensors
12:15–12:30	SC06	**Alice Marinangeli** Molecularly Imprinted Nanoparticles and Time-Resolved Fluorescence for the Detection of Protein Contaminants
12:30–12:45	SC07	**Dominik Korol** Chemosensing on Cost-Effective Substrates – a Flexible MIP-Based Chemosensor for Selective Detection of Metronidazole
12:45–13:00	SC08	**Vu Bao Chau Nguyen** MIP-Based Electrochemical Sensors Detecting Antibiotics and Fungicides as Emerging Contaminants in Aqueous Environments
13:00–13:15	SC09	**Christos Galanos** Molecularly Imprinted Polymers for the Selective Recognition and Immobilization of Microorganisms
13:15–14:45		**Group Photo & Lunch**

14:45–16:15		**Afternoon session 1** Chairs: C. Kranz / Ł. Półtorak
14:45–15:05	K16	**Martin Jönsson-Niedziółka** Sequential Microfluidic Device for Point-of-Care Electrochemical Detection of C Reactive Protein Based on a Novel Peptide
15:05–15:25	K17	**Paweł Niedziałkowski** Gold Nanocubes (AuNCs) – Synthesis, Characterization and Selection of a Relevant Surface Modification – for Biosensing Application
15:25–15:45	K18	**Nataliya Stasyuk** Nanozymes as Functional Elements of Biosensors
15:45–16:00	SC10	**Maciej Cieplak** Electroactive Molecularly Imprinted Polymer Nanoparticles for Selective Glyphosate Determination
16:00–16:15	SC11	**Zahra Akbari** AuNP-Enhanced Schiff Base Nanocomposites for Lead (II) Ion Sensing in Seawater
16:15–19:00		**Social event**
19:00–22:00		**Gala dinner**

Monday, November 6

08:00–09:00		**Breakfast**
09:00–10:40		**Morning session 1** Chairs: M. Wiloch / F. Marken
09:00–09:45	T05	**Gary Blanchard** The Piezoelectric Effect in Ionic Liquids. Mechanistic Insights and Sensing Applications
09:45–10:05	K19	**Catherine Branger** Towards Novel Sensing Receptors Based on Modified Gold Electrodes by Active Molecularly Imprinted Polymers
10:05–10:25	K20	**Paweł Krysiński** Iron Oxide Superparamagnetic Nanoparticles for the Adsorption and Photocatalytic Degradation of Pharmaceutics. Tetracycline Case
10:25–10:40	SC12	**Juliana Cancino-Bernardi** Cell Membranes Used as Biorecognition Element to Impedimetric Biosensing
10:40–11:10		**Coffee break**
11:10–12:55		**Morning session 2** Chairs: S. Grecchi / M. Jönsson-Niedziółka

11:10–11:30	K21	**Ilaria Palchetti** Microfluidic Procedure for the Electrochemical Biosensing of Isothermally-Amplified DNA
11:30–11:50	K22	**Sabine Kuss** Disease Detection at the Microscale – Cytochrome C Oxidase Deficiency Quantification in Human Fibroblasts
11:50–12:10	K23	**Jacek Ryl** Multivariate Data Analysis of Multisine Impedimetric Fingerprints in Electroanalysis of Biochemical Compounds
12:10–12:25	SC13	**Krzysztof Noworyta** Biphenol Selective Electrosynthesis on the Molecularly Imprinted Polymer-Coated Electrodes
12:25–12:40	SC14	**Parastoo Vahdatiyekta** Synthesis and Application of BTMDs in E-Tongue for Detecting Homovanillic Acid: a Potential Breast Cancer Biomarker
12:40–12:55	SC15	**Alexandra Canciu** Electrochemical Aptamer-Based Sensors for the Label-Free Detection of Pathogen Bacteria
13:15–14:45		**Lunch**
14:45–16:20		**Afternoon session 1** Chairs: S. Kuss / K. Noworyta
14:45–15:05	K24	**Wojciech Nogala** Analysis of Heterogeneous Hydrogen Evolution with Scanning Electrochemical Microscopy
15:05–15:25	K25	**Christine Kranz** Surface Modification via Scanning Electrochemical Probe Microscopy (SEPM): from Molecular Catalyst Arrays to Antimicrobial Surfaces
15:25–15:45	K26	**Jean-Marc Noël** Unraveling the Mechanism of Aryldiazonium Reduction: Evidence and Quantitative Analysis of Reactive Intermediates and Byproducts
15:45–16:05	K27	**Vitali Syritski** Electrochemical Sensing of Clinically Relevant Proteins by Molecularly Imprinted Polymer-Modified Electrodes
16:05–16:20	SC16	**ST Balamurugan Thangaraj** Electroanalytical Screening of Clozapine (Date and Rape Drug) in Soft and Hard Drinks at Electrified Liquid-Liquid Interfaces
16:30–17:00		**Coffee break**
17:00–18:15		**Afternoon session 2** Chairs: J. Kochana / L. Jeuken
17:00–17:20	K28	**Bartłomiej Graczykowski** Mechanical and Thermal Engineering of Functional Nanomembranes

17:20–17:40	K29	**Emilia Witkowska-Nery** Simple Systems for Electrochemical Ion Sensing
17:40–18:00	K30	**Łukasz Półtorak** Drugs, Membranes, 3D Printing and Sensing at Electrified Soft Junctions
18:00–18:15	SC17	**Julia Maciejewska-Komorowska** Transfer of Sulfate Ions Between Immiscible Liquids at the Three-Phase Junction Using a Novel Compound
19:00–20:00		**Dinner**
21:00–3:00		**Disco**

Tuesday, November 7

08:00–09:00		**Breakfast**
09:00–10:40		**Morning session 1** Chairs: E. Witkowska-Nery / P. Niedziałkowski
09:00–09:45	T06	**Sławomir Sęk** Exploring Surface Films of Peptides and Oligourea Foldamers for Material Applications and Molecular Switching
09:45–10:05	K31	**Piotr Pięta** Size-Dependent Effects of Amyloid Beta (Aβ) on a Model Brain-like Membrane
10:05–10:25	K32	**Lars Jeuken** Hybrid Polymer-Lipid Membrane Modified Electrodes
10:25–10:40	SC18	**Mostafa Torabi** Electrochemistry of Proteoliposome Derived Lipid Bilayers: HMG CoA Reductase and its Inhibition by Statins
10:40–11:10		**Coffee break**
11:10–11:45		**Morning session 2** Chairs: S. Arnaboldi / S. Sęk
11:10–11:30	K33	**Yolina Hubenova** Metabolic Pathways' Components Participating in the Cellular Response of a Biofilm to the Electrode Polarization
11:30–11:45	SC19	**Rafał Zbonikowski** Interfacial Colloidal Stimuli-Responsive Composed of Nanoparticles Decorated with Poly(N-Isopropyl Acrylamide) (PNIPAM)
11:45–12:00		**Closing ceremony**
12:00–13:00		**Lunch**
13:30		**Departures**

T01

Gold Clusters Doping Lipid Layer Act as Remote Nanoelectrodes towards Electroactive Probes

Renata Bilewicz, Agnieszka Wieckowska, Elzbieta Jablonowska, Marcin Jaskolowski

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We return to the discussion of electron transport across insulating thin films on electrodes.[1–4] Instead of alkanethiol or polymer films, we use the combined Langmuir-Blodgett-Schaefer technique to construct a lipid DPPTE or DPPTE/DOPC layer at the gold substrate. Metal nanoparticles have often been added to various films covering the electrodes to increase their conductivity. We demonstrate that gold clusters (AuNCs) can play the role of remote gold electrodes transferring electrons to the solution species when they are added to the external monolayer of the lipid bilayer transferred in the Langmuir-Schaefer (horizontal touch) step of the combined method. The electrode processes of hexaammineruthenium(III) and hydrogen peroxide are chosen to probe the changes of the AuNCs-doped lipid film covering the gold substrate. In the presence of the gold clusters, no inhibition of electron transfer to the electrode was observed as long as the film was sufficiently thin to provide electronic contact of the gold clusters with the gold substrate. Reversibility of the hexaammineruthenium(III) process is restored when as low as 0.01% Au clusters are dispersed in the outer leaflet of the lipid bilayer.

With the increasing thickness of the film separating the clusters from the electrode, the electronic coupling with the electrode was lost, and the lipidic film restored its efficient barrier properties despite the presence of AuNCs in the external lipid monolayer. The lipid-inorganic hybrid system described here is promising for application in electroanalytical and biocatalytic sensing. The film-covered electrode would decrease the difficulties connected with the adsorption of unwanted solution species on the electrode while preserving the required sensitivity of the sensor.

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2 J.N. Chazalviel, P. Allongue, *J. Am. Chem. Soc.*, 2011, 133, 762–764.
3 S.A. Shermukhamedov, R.R Nazmutdinov, T.T Zinkicheva, M.D. Bronshtein, J. Zhang, B. Mao, Z. Tian, J. Yan, D-Y. Wu, J. Ulstrup, *J. Am. Chem. Soc.*, **2020**, *142*, 10646–10658.
4 A. Wieckowska, E. Jablonowska, M. Dzwonek, M. Jaskolowski, R. Bilewicz, *ChemElectroChem*, **2022**, *9*, e202101367.

K01

Coupling Ionic Diodes in Membranes for Desalination and Electroosmotic Water Transport

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Ionic diodes switch between an open state (ionic current flow) and a closed state (no ionic current) depending on the applied potentials. There are different types of mechanisms and ionic diodes, for example, based on nanopores,[1] chemical processes, or based on microholes coated with ionomers.[2] An ionic diode can act as a rectifier, but only when coupling ionic diodes to circuits[3] can useful processes be designed.

Coupling a cationic diode with an anionic diode links cation transport to anion transport. With an alternating current (AC) driver electrode, this leads to salination and desalination processes[4] similar to those in electrodialysis but without generating side products. Coupling two anionic diodes for different ionomer materials produces (under AC driving conditions) a net zero ion current but an associated electroosmotic transport of water (solvent). This process is closely related to reverse osmosis (a major water purification process) but without any external driver pressure. These mechanisms are based on membrane-internal phenomena driven by externally applied alternating potentials.

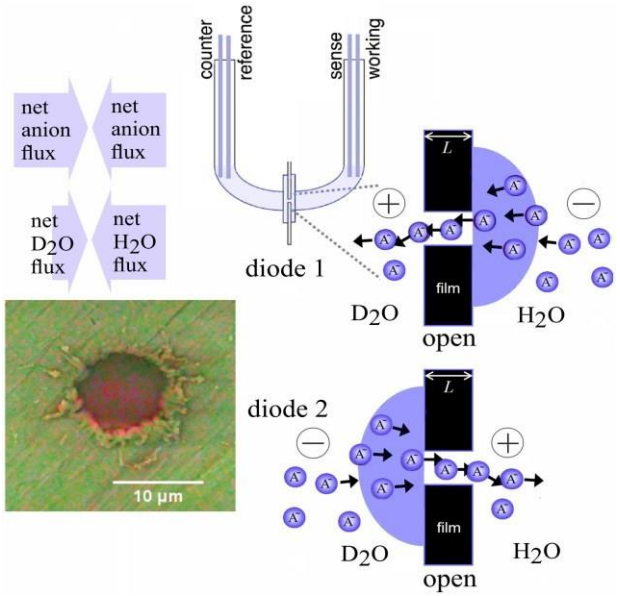

Figure 1. Experimental scheme for a 4-electrode ionic diode; scanning electron micrograph with elemental mapping colours showing an ionic diode with 10 µm diameter; schematic explaining AC-electroosmotic water pumping with two coupled anionic diodes.

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SC01

Spectroelectrochemical Studies of a Potential Drug Against Alzheimer's Disease

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Alzheimer's disease (AD) is the most common cause of dementia amongst the elderly, yet it remains incurable. Understanding how AD develops is crucial to finding a cure. One hypothesis is that peptides from the β-amyloid (Aβ) family are responsible for AD development. Until now, the most studied amyloids are Aβ(1–*x*) (where *x* = 16, 40, or 42 amino acids). Aβ(1–*x*) binds copper(II) ions, and under the conditions prevailing in the human body, ascorbic acid causes the reduction reaction Cu(II)-Aβ(1–*x*)/Cu(I)-Aβ(1–*x*) which leads to the formation of reactive oxygen species and reactive nitrogen species. ROS and RNS are compounds highly toxic to nerve cells.

Therefore, substances that can aid in removing copper(II) ions from β-amyloids could block the formation of ROS and RNS. Recently, a new quinoline derivatives with unique properties have been discovered. However, little is known about the redox properties of such molecules, which may be crucial in the early stages of testing potential therapeutic substances.

Therefore, we aimed to perform studies of a TDMQ20 whose redox properties were not yet well tested. To fully characterize both anodic and cathodic processes, we used cyclic and pulse voltammetry over a wide range of pH values, including physiological (pH = 7.4). In addition, the experimental results were supported by spectroscopic studies aiming to follow the deportation of TDMQ20 and to study the formation of complexes with copper(II) ions.

The kind of electrochemical tests presented here may prove crucial importance for the development of more effective drugs against AD. The high failure rate and relatively poor performance of the recently approved treatment indicate the need to extend preclinical studies with new, so far unused techniques, allowing a more complete picture to be obtained of the effectiveness and toxicity of the potential drug candidates.

Acknowledgments:
This work has been financially supported by the National Science Centre Poland within the Sonatina project 2021/40/C/ST4/00090.

Saturday, November 4

08:00–09:00		**Breakfast**
09:00–10:40		**Morning session 1** Chairs: V. Ostatná / W. Nogala
09:00–09:45	T02	**Alexander Kuhn** Bipolar Nanoelectrochemistry for Controlled Surface Modification
09:45–10:05	K02	**Serena Arnaboldi** Electromechanical Systems for the Enantioselective Wireless Loading and Release of Fluids
10:05–10:25	K03	**Fred Lisdat** Recent Progress in Coupling Photoactive Protein Complexes to Electrodes
10:25–10:40	SC02	**Mario Mitov** Simultaneous Gold and Silver Recovery in Microbial Fuel Cells Operating in a Short-Circuited Mode
10:40–11:10		**Coffee break**
11:10–13:05		**Morning session 2** Chairs: A. Canciu / J. Ryl
11:10–11:30	K04	**Larysa Baraban** Nanoelectronics for Cancer Therapy
11:30–11:50	K05	**Elena Ferapontova** Interfacial Design of Electrocatalytic DNA- and Aptasensors
11:50–12:10	K06	**Mathieu Etienne** Nicotinamide Cofactor – Dihydrogen Interconversion for Electrosynthesis
12:10–12:30	K07	**Svyatoslav Kondrat** The Role of Quantum Capacitance in Capacitive Energy Storage with Low-Dimensional Electrodes
12:30–12:50	K08	**Liang Liu** Scanning Gel Electrochemical Microscopy for Surfaces Examination and Modification towards Biological Applications
12:50–13:05	SC03	**Adrian Olejnik** Structure and Photoelectrochemistry of the Laser-Graphitized Polydopamine Coating
13:15–14:45		**Lunch**
14:45–16:20		**Afternoon session 1** Chairs: E. Ferapontova / P. Pięta

14:45–15:05	K09	**Chloé Grazon** From Quantum Dots to Fluorescent Organic Nanoparticles: Bright Nanotools for Biosensing
15:05–15:25	K10	**Andreas Lesch** Print-Light-Synthesis for Large-Scale Fabrication of Metal Films for Electrochemical Sensing
15:25–15:45	K11	**Insung Choi** Single-Cell Nanoencapsulation: Past, Present, and Future
15:45–16:05	K12	**Ambra Giannetti** Signal-Off SERS Biosensor Based on a Molecular Beacon for miRNA Detection
16:05–16:20	SC04	**Maria Madej** Voltammetric Biosensor Based on Horseradish Peroxidase and MOF JUK-2 for 17-β-Estradiol Determination
16:30–17:00		**Coffee break**
17:00–19:00		**Poster session**
19:00–20:00		**Dinner**

T02

Bipolar Nanoelectrochemistry for Controlled Surface Modification

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Bipolar electrochemistry (BPE) is a concept based on the fact that two opposite chemical processes, oxidation and reduction, occur simultaneously on the surface of a (semi)conducting object without a physical connection to a power supply.[1] The approach has gained increasing attention during the last two decades, as it can be used for various applications, ranging from materials science and (bio)electroanalysis,[2–4] to the generation of motion and electrocatalysis.[5–9]

However, the equations describing the fundamentals of BPE predict that wireless electrochemical addressing gets increasingly difficult for objects with small dimensions.

There are several strategies to circumvent this apparent problem and to achieve controlled surface modification of nanoobjects. The first obvious option is to apply very high potential differences between the feeder electrodes, but specific equipment, such as a capillary electrophoresis set-up, is needed in this case.[10] An interesting alternative is light-assisted BPE,[11] which allows addressing micro- and nanoobjects.[12,13] An additional option is to carry out experiments in confined environments, such as 2D liquid layers.[14–16] In this case, parasitic currents are minimized, and thus, it is possible to modify nanoobjects, e.g., single layers of graphene, in a very well-controlled way.[17]

These different approaches illustrate that there are plenty of possibilities to use the attractive features of BPE in the frame of nanoscience and to perform surface modification experiments that simply are not possible with conventional electrochemistry.

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K02

Electromechanical Systems for the Enantioselective Wireless Loading and Release of Fluids

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Chirality plays an important role in multiple fields of science, such as chemistry, biology, or medicine. Although enantioselective separation of chiral molecules, induced by external stimuli, has been well established,[1] the development of miniaturized chiral soft systems able to quickly and wirelessly distinguish such molecules still faces great challenges. The synergy between the mechanical properties and the enantioselectivity of conjugated polymers powered by bipolar electrochemistry (BE) could lead to so far unexplored effects. Through this approach, we have prepared soft tubes[2] and actuators[3] that mimic either chiral columns or chiral valves commonly used in the field of chiral chromatography and microfluidic, respectively. Furthermore, the wireless mode, an intrinsic feature of BE, is an added value that allows the recognition and/or separation of chiral molecules cheaply and quickly.

Acknowledgments:
This work has been funded by the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (grant agreement no 741251, ERC Advanced grant ELECTRA) and the HORIZON-ERC-2021 work program (grant agreement no 101040798, ERC Starting grant CHEIR).

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K03

Recent Progress in Coupling Photoactive Protein Complexes to Electrodes

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Photobioelectrodes have become an interesting new research field that follows the idea of coupling catalytically active protein molecules to electrodes, such as in the field of enzyme sensors. Different photo-active protein complexes and a diverse number of materials and surface modifications have already been studied, resulting in significant progress in this field.

The presentation will give an overview of the properties of photoactive complexes from a thermophilic bacterium, which have been exploited for efficient protein-electrode coupling. It will start with a careful analysis of reaction conditions of natural partners of photosystems I and the transfer of this knowledge to the construction of photobioelectrodes.[1–3]

Here, one focus is on the electrode structure, which should not only allow an efficient electron transfer but also the harboring of larger amounts of protein.[3–5] Transmission and electrode thicknesses are key features here. The performance can be further enhanced when two light-sensitive components can be coupled to the electrode structure.[6]

As for electron transfer, different modes can be exploited – the first focus is following the natural example and using a small redox protein, although it is not a natural partner, and building a mediator-based system.[2–5] Another direction deals with the possibilities of direct electron exchange, which is also possible with these rather large protein complexes.[8–10]

Furthermore, it can be shown that a modification of the photoactive proteins can be beneficial with respect to an improved light interaction but also with respect to the electrode communication.[9]

Finally, the aspect of electron donors or acceptors in solution will also be illustrated. In the case of photobiocathodes, the acceptor oxygen can beneficially be replaced by other species.[5–10] Particularly attractive are enzyme reactions, which need to be fed by electrons. Here, photocurrent generation can be advantageously coupled to the biocatalytic production of a valuable substance.

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SC02

Simultaneous Gold and Silver Recovery in Microbial Fuel Cells Operating in a Short-Circuited Mode

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The recovery of precious metals from various industrial waste streams and end-of-life commercial products is the only way to balance the growing gap between their demand and production. Most of the currently applied methods and technologies for metal recovery are energy-intensive and use expensive and toxic chemicals, causing additional environmental pollution. Recently, we demonstrated for the first time a novel bioelectrochemical approach for metal recovery.[1–3] The method is based on the principle of the microbial electrochemical snorkel (MES), providing the highest rate of the ongoing processes in the bioelectrochemical reactor without adding energy and reagents. In this study, simultaneous gold and silver recovery from Au(I)- and Ag(I)-dithiosulfate complexes by MES is proven. The proof of concept was demonstrated by short-circuiting a graphitized paper (GP) cathode immersed in a mixed solution of gold and silver dithiosulfate complexes with a sediment microbial fuel cell bioanode, both placed in a vertical reactor. Within 24 h, both metals were completely depleted from the catholyte, and the cathode was decorated with globular nanosized deposits absent in the control. The energy-dispersive X-ray spectroscopy, powder X-ray diffraction, and X-ray fluorescence analyses confirmed the presence of gold and silver in the obtained deposits, and the results from X-ray photoelectron spectroscopy revealed that both metals were in an elemental state. Additional electrochemical tests performed on the fabricated Au-Ag/GP modified electrodes in a neutral electrolyte showed that they possess higher intrinsic catalytic activity towards the hydrogen evolution reaction than Au/GP and Ag/GP alone, revealing their potential application as cathodes in microbial electrolysis cells.

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K04

Nanoelectronics for Cancer Therapy

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Novel strategies for on-chip integrated nanoelectronic devices inspired the development of a new generation of biosensors employing inorganic and organic materials. The main element of such biosensors is a semiconductor (e.g., in field-effect transistors) or metal (in electrochemical, chemiresistive, or impedimetric sensors) transducer, with the radically miniaturized sensing area down to several nanometers. Merging such nanodevices with biological species, e.g., cells or molecules of similar nanosizes, offers a remarkable increase in biosensor sensitivity. When combined with microfluidic technology, this approach relies on the measurement of the electrical response of the device, such as current, voltage, or electrical impedance, for monitoring low titration levels (down to femtomolar levels) of diverse biomolecules in physiological fluids.

Despite this success, nanobioelectronics is still underrepresented in the field of oncology. While the research area has addressed their potential applications in early cancer diagnosis, less effort has been dedicated to therapy development and patient monitoring (Figure 1, B). In this area, potential use cases are limited mainly by liquid biopsy, detection of circulating tumor cells, or circulating tumor DNA. Here, we review some of the important contributions to the field of nanobioelectronics when applying it to cancer research. In particular, the implementation of so-called silicon nanowire-based field effect platforms and extended gate-based systems for ultrasensitive detection of cancer-related biomarkers and cancer-related therapy will be discussed.

In conclusion, by observing the development of the research field in recent years, one can state that nanoelectronics has a high potential to be better represented in cancer research in the near future and to facilitate the transition from conventional medicine to precision medicine in clinical oncology (Figure 1, A). In particular, nanoelectronics can open new routes to perform a complex combinatorial analysis using tiny electronic chips and simultaneously screening multiple biochemical species.

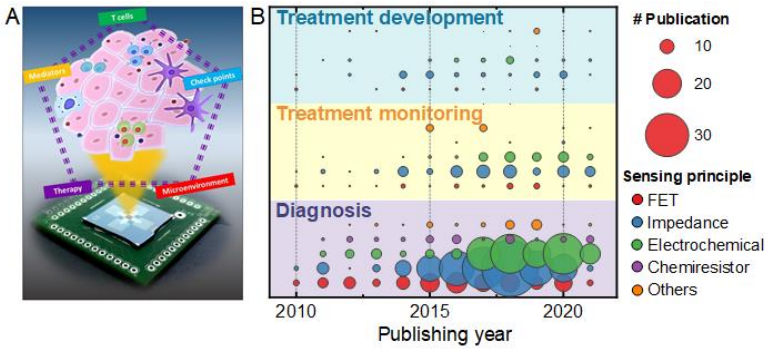

Figure 1. (A) Use of the nanoscopic elements for the characterization of the cancer and (B) overview of the research field and application of the biosensors in the field of cancer research.

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K05

Interfacial Design of Electrocatalytic DNA- and Aptasensors

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Unique bio-recognition and electron transfer (ET) properties of nucleic acids are extensively used in sensitive, accurate, yet inexpensive bioelectroanalytical platforms. Bio-recognition can be read out via reactions of DNA with redox indicators specifically interacting with single- and double-stranded DNA[1] and via electrochemistry of redox-labeled DNA that depends on the surface architecture of the individual DNA molecules.[2] Electrochemical aptamer-based assays similarly depend on interfacial and electronic properties of the aptamers.[3] Along with that, a 1:1 stoichiometry of bio-recognition challenges the ultra-low concentration analysis and calls for signal amplification, while non-specifically adsorbing media components demand antifouling bio-interfaces.

Here, I discuss the interfacial state and structure of the electrode-tethered DNA and electrode reactions facilitated in such systems, including DNA-mediated long-range electron transfer and reactions proceeding in redox-labeled DNA.[4] I overview our research on electrocatalytically amplified assays for bacteria and cancer biomarker human epidermal growth factor receptor 2 (HER2) and thrombin, all avoiding interference from serum components by the careful designs of the antifouling interface additionally enabling electrocatalytic signal amplification either by the ferricyanide/methylene blue couple[5,6] or O_2-dependent covalent G4-hemin complexes.[7–9] Perspectives of inexpensive aptamer ELASA devices for liquid biopsy analysis will be discussed.

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K06

Nicotinamide Cofactor – Dihydrogen Interconversion for Electrosynthesis

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This keynote will present recent research on nicotinamide-hydrogen cofactor interconversion for electrosynthesis.

NADH and NADPH are enzymatic cofactors used by a large number of enzymes for hydride transfer in a wide range of biochemical reactions. After this transfer, NAD^+ or $NADP^+$ molecules are produced and must be regenerated.

When considering the biotechnological application of the NAD(P)-dependent enzyme for producing fine chemicals or even the reduction of CO_2, it is essential to regenerate the reduced form of the cofactor.

Electrochemical methods and cells enable cofactor regeneration with high efficiency and productivity. I will discuss recent advances in this field, focusing on using dihydrogen as a source of electrons and protons for electroenzymatic synthesis.

K07

The Role of Quantum Capacitance in Capacitive Energy Storage with Low-Dimensional Electrodes

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Low-dimensional electrode materials are gaining increasing importance in capacitive energy and conversion.[1] A characteristic signature of such electrodes is the presence of quantum (or space-charge) capacitance, which arises due to the finite density of states of electrons in an electrode; this is in contrast to ideally metallic electrodes, where this capacitance is infinite. In a pioneering study, Gerisher[2] demonstrated that quantum capacitance, rather than electrical double-layer capacitance, governs the total measured capacitance of an electrolyte at graphite electrodes. Subsequent research has indicated that quantum capacitance tends to have a detrimental effect, leading to a reduction in the total capacitance.[3,4] However, these studies have predominantly focused on flat electrodes and carbon nanotubes (CNTs) with an electrolyte surrounding the CNTs.

In this lecture, I discuss the impact of quantum capacitance on the capacitive properties of narrow nanotubes filled with an electrolyte. We employ analytically solvable and computationally efficient yet realistic models,[5,6] allowing us to systematically explore the effects of quantum capacitance. Aligned with previous research, we find that quantum capacitance lowers total capacitance compared to capacitance associated with ideally metallic nanotubes.[7] However, this reduction is primarily observed at low potential differences applied to a nanotube relative to the bulk electrolyte. At intermediate and high potential differences, where a CNT becomes saturated with counter-ions, low quantum capacitance can actually enhance energy storage. This enhancement can be quite substantial, resulting in a few-fold increase in stored energy density. Our results suggest exciting opportunities for boosting capacitive energy storage through judicial engineering of the electronic properties of low-dimensional electrodes.[7]

Acknowledgments:
This work was supported by NCN grants No. 2020/39/I/ST3/02199 and 2021/40/Q/ST4/00160.

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K08

Scanning Gel Electrochemical Microscopy for Surfaces Examination and Modification towards Biological Applications

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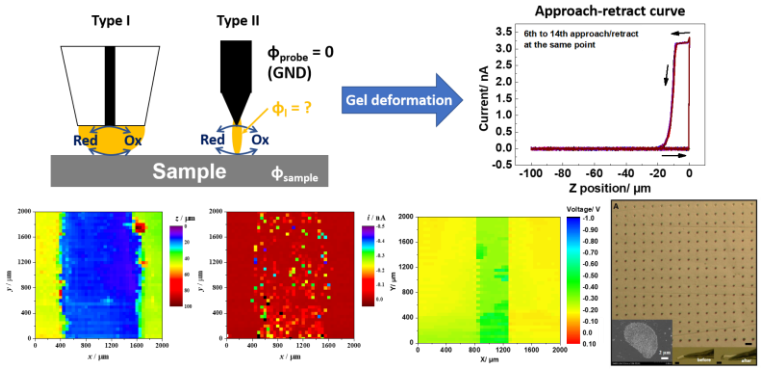
Scanning electrochemical probe techniques have been developed in the last 30 years for measuring spatially localized electrochemistry at micro and nano scale. Here, we will present a recently developed tool, namely Scanning Gel Electrochemical Microscopy, for imaging the electrochemical reactivity of surfaces and patterning surfaces by local electrodeposition. The concept is based on a gel probe that is in soft contact with the sample, allowing electrochemical measurements to be spatially localized in the contact area with gel as electrolyte.[1] The physical resolution, or the pixel size, can thus be tuned by pressing or pulling the probe after touching the sample.[2] So far, two types of gel probes have been developed: Type I by electrodeposition of chitosan on micro-disk electrodes,[1-3] and Type II by "electrodeposition + pulling" on sharpened metal wires.[4] Local chronoamperometry, potentiometry and cyclic voltammetry have been carried out, either for imaging or for patterning (complex-shaped) surfaces.[1–4]

The gel has an advantage of localizing and immobilizing the electrolyte, which "frees" the sample from solution in scanning electrochemical microscopy (SECM) and reduces the wetting in scanning electrochemical cell microscopy (SECCM) as supported by quartz crystal microbalance (QCM) measurements in our recent work.[5] Moreover, the approach-retract curves may reveal the deformation of the gel, which could reflect the mechanical changes of the gel-sample interface. All these, together with the excellent biocompatibility of chitosan, make SGECM a promising technique for biological applications. Prospects include immobilizing drugs, proteins or bacteria in the gel probe and studying their chemical and mechanical interactions with biological samples such as cells cultured in agar plate. Our ongoing effort focuses on the quantitative analysis.



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SC03

Structure and Photoelectrochemistry of the Laser-Graphitized Polydopamine Coating

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The idea of the PDA laser graphitization was published in 2019 in Nature Communications.[1] Initially, the main objective of the modification was the enhancement of mechanical properties so that the PDA acquires higher resistance to abrasions and scratches. However, none of the existing works elaborated on the photoelectrochemical properties and electronic structure of the laser graphitized PDA (lgPDA) and its behavior in the junction with inorganic semiconductors.

In the following work, PDA is electropolymerized on the surface of titania nanotubes (TNTs), and the protocol for laser graphitization using Nd:YAG nanosecond pulsed laser is developed. Graphitization is confirmed by XPS and Raman spectroscopies, and nanoindentation and water contact angle measurements were carried out. The variety of the laser treatment parameters (wavelength, pulse energy, and number of pulses) is screened to establish structure-property relations and further optimized towards the highest photocurrent generation in the visible spectrum or the highest electrochemical activity measured by the redox probe.

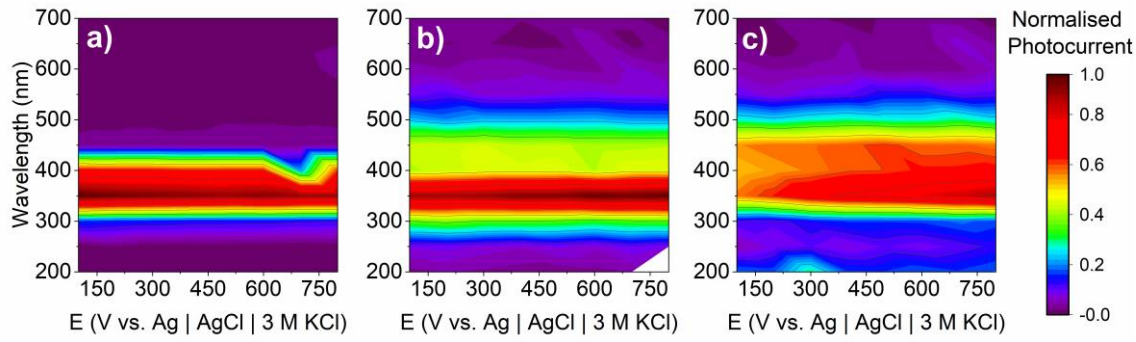

Figure 1. Photocurrent maps of the a) pristine TNTs, b) TNT_PDA, and c) TNT_lgPDA.

Acknowledgments:
This research was funded via the National Science Center (Preludium) 2022/45/N/ST5/00192 and the Ministry of Education and Science (Diamentowy Grant) DI2019 017964 grants.

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K09

From Quantum Dots to Fluorescent Organic Nanoparticles: Bright Nanotools for Biosensing

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Förster resonance energy transfer (FRET) is a widely used and ideal transduction modality for fluorescent-based biosensors, offering a high signal-to-noise ratio with a visibly detectable signal. While intense efforts are ongoing to improve the limit of detection and dynamic range of biosensors based on biomolecule optimization, the nature and relative location of the dye remain understudied.

Herein, the first part of the presentation will be dedicated to a comparison of the nature of the dye, i.e., organic fluorophore (Cy5 or Texas Red) vs. inorganic nanoparticle (QD) and the position of the FRET donor or acceptor on the bioreceptor.[1,2] Using a recently discovered transcription factor (TF) – DNA biosensor for progesterone,[3] four different biosensor configurations are examined, and the quantum yield, lifetime, FRET efficiency, IC50, and limit of detection are reported. The key molecular parameters driving the sensor performances in each biosensor configuration are thus identified, and a set of design parameters is provided to enable one to select the fluorophore system for their future FRET assays and new diagnostic devices.

In the second part of the talk, fluorescent organic nanoparticles (Dye-FONs)[4] will be introduced as a metal-free alternative to the QDs while maintaining a comparable brightness per volume. Dye-FONs are single-component fluorescent organic nanoparticles obtained from the nanoprecipitation of dedicated hydrophobic organic dyes assembled in water. Despite the growing interest in dye-FONs for various biological applications,[5] the strategies deployed to functionalize their surface and to use them as biosensors are still very limited. Current options to obtain functionalizable FONs are mainly to perform the nanoprecipitation of the dye concomitantly with an amphiphilic copolymer or to coat the FONs with a polymer after the nanoprecipitation. However, when affecting these two approaches, the polymer on the FON surface increases the nanoparticles hydrodynamic diameter, which can be detrimental when developing FRET-type biosensors where the sensing dye has to be in close proximity to the fluorescent nanoparticle. To overcome those limitations, we propose an original approach based on direct dye-functionalization. As such, original maleimides push-pull hydrophobic dyes are synthesized and nanoprecipitated to obtain functionalizable nanoparticles in water directly. The efficient surface grafting with a thiolated molecule is proven using the well-known bio-active biotin.

Acknowledgments:
CG deeply acknowledges her main collaborators who permitted her to develop those studies, especially M.W. Grinstaff, J. Gallagan, A.M. Dennis, S. Lecommandoux, M. Chern, O. Dal Pra, J. Daniel, and M. Blanchard-Desce. This work received support from the EU under the H2020 program (Marie-Curie Grant 749973) and the Horizon Europe program (ERC St 101077364).

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K10

Print-Light-Synthesis for Large-Scale Fabrication of Metal Films for Electrochemical Sensing

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Commercial electrochemical biosensors are aimed to be fabricated and operated at low costs. For this purpose, the sensing platform is based on screen-printed or photolithographically fabricated conductive films made of graphite, gold, or platinum that are chemically modified to provide and enhance sensitivity and selectivity for electroanalytical detections. Both screen-printing and photolithography are mask-based fabrication techniques, reducing the flexibility for rapid electrode design and electrode design modification (including pattern shapes, material loadings, and sensor dimensions), which is particularly important during the sensor development and prototyping phases. Cost reduction is only achieved when large numbers of sensors are prepared, which is often unrealistic for small-scale academic research projects. Inkjet printing is mask-less and enables rapid design changes and high control of the material amounts printed by the ink composition and numbers of droplets deposited per area, but it suffers from the instability of nanoparticle dispersions that irreversibly block the printhead nozzles. This limitation is one main obstacle that still hinders the technological breakthrough of inkjet printing in sensor manufacturing. The fabrication of metal thin films by ink-based printing technologies is traditionally a two-step process in which i) a metal nanoparticle (NP) ink, based on previously synthesized and purified NPs, is deposited on a substrate by inkjet- or screen- printing and then ii) thermally treated to obtain the desired solid films. For several years, we have worked on the efficient merging of nanoparticle synthesis and metal film printing into a single process.

The one-step fabrication of metal thin films by combining inkjet-printing of metal precursor inks and the simultaneous photochemical conversion of the metal precursors into metal NPs is known as Print-Light-Synthesis (PLS) and will be presented in this lecture. PLS is characterized by its high flexibility of the process parameters, enabling the fabrication of thin conductive metallic films and coatings of individual metal NPs. PLS is economically attractive as it produces sensors without material waste, and the production costs are reasonably low, even at low production volumes. It is further attractive for research and development, as it is very flexible regarding material selection and surface characteristics to be obtained. In particular, the fabrication of gold thin film electrodes will be presented, and the advantages of PLS Au electrodes over commercially available screen-printed Au electrodes will be discussed. Finally, we will present the fabrication of conductive film electrodes, also made of metals, which at first glance, are unusual for electrochemical sensing but become interesting due to the opportunities that PLS provides for sensor research, development, and applications.

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K11

Single-Cell Nanoencapsulation: Past, Present, and Future

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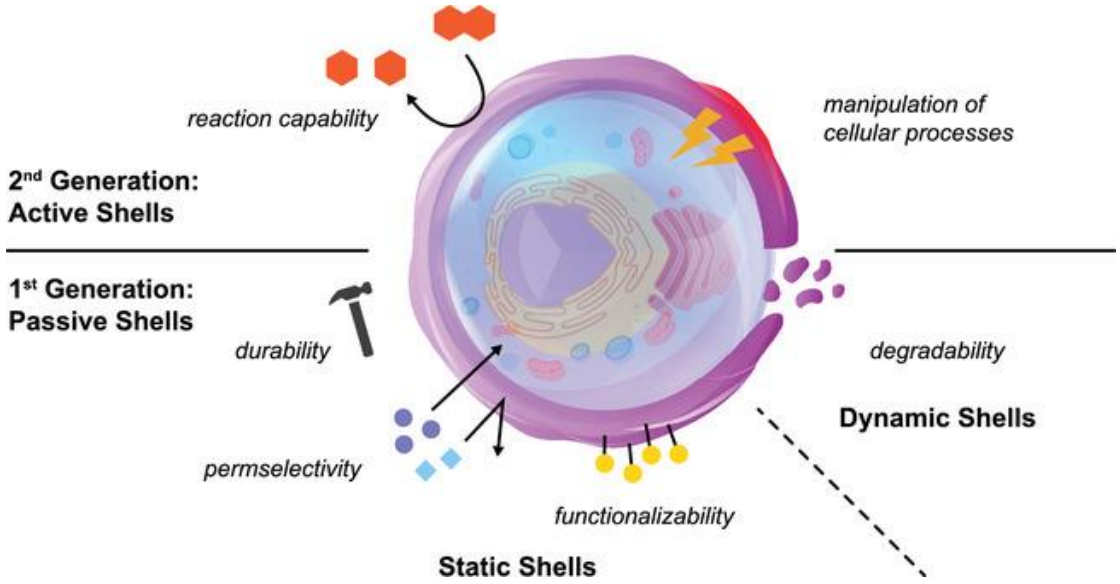
Single-cell nanoencapsulation (SCNE) is a cytocompatible chemical strategy that physically confines individual living cells within ultrathin (preferably <100 nm) tough shells in three-dimensional space.[1–3] The cellular nanobiohybrid structures created by SCNE have been referred to by various names, such as cell-in-shell structures, artificial spores,[4,5] micrometric Iron Men,[6] and micrometric Transformers. Since the concept was first introduced in 2013, the field of SCNE has rapidly grown and recently entered its second stage of development, in which the artificial shells play complementary but active roles in the innate cellular metabolism and activities beyond merely providing protection against harmful external agents.[7] This talk discusses a concise overview of the past, present, and future of SCNE.



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K12

Signal-Off SERS Biosensor Based on a Molecular Beacon for miRNA Detection

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In the last years, due to its high sensitivity, surface-enhanced Raman scattering (SERS) has opened exciting new routes for many biosensing applications for biomarker detection.

Among all biomarkers, scientists are increasing their interest in microRNAs (miRNAs), which have the potential to impact the development and progression of nearly all human diseases through interactions with mRNA. The strategy exploited in this work for miRNA detection is a signal-off mechanism (Figure 1) by means of a labeled molecular beacon (MB)[1] immobilized on a SERS substrate as the miRNA biorecognition element: the MB tagged with a Raman reporter was employed, and the distance between the label and the SERS surface distinctly changed upon hybridization with miRNA, resulting in a large measurable SERS signal change.

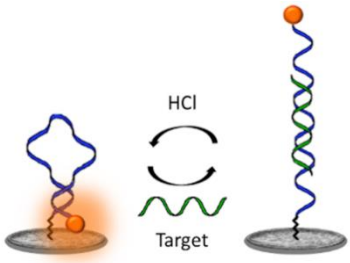

Figure 1. Mechanism of operation and reversibility of the MB-decorated SERS nanosensor for miRNA target.

After characterization in fluorescence, the MB labeled with the Raman tag was exploited for miRNA SERS biosensing by using a multi-well liquid cell adapted for the SERS measurements. In order to maximize the SERS signal while ensuring the advantages of a cost-effective and practical assay, we developed a plasmonic platform based on a SERS substrate specifically designed to increase the local molecular density at the SERS hotspots and produced from a network of silver nanowires (AgNWs).[2]

Sub-femtomolar detection limits for miRNA-183 were obtained with this approach after optimization of the sensing surface. Good specificity and the possibility of performing multiple cycles of measurements after regeneration were also demonstrated.

Acknowledgments:
This research was produced with the co-funding European Union – Next Generation EU, in the context of The National Recovery and Resilience Plan, Investment Partenariato Esteso PE8 "Conseguenze e sfide dell'invecchiamento", Project Age-It (Ageing Well in an Ageing Society) and EU project ECS00000017 'Ecosistema dell'Innovazione' Tuscany Health Ecosystem (THE, PNRR, Spoke 4: Nanotechnologies for diagnosis and therapy).

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SC04

Voltammetric Biosensor Based on Horseradish Peroxidase and MOF JUK-2 for 17-β-Estradiol Determination

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Sex hormones, like estrogens, play a crucial role in the proper development and functioning of reproductive organs in the human body. Among estrogens, 17-β-estradiol (E2) levels are most commonly monitored in medical diagnostics in order to assess irregularities in the menstrual cycle, fertility issues, menopause, as well as osteoporosis. Frequent blood sampling is burdensome for patients; therefore, methods enabling non-invasive analysis of E2 from saliva and urine are gaining importance.[1] Electrochemical biosensors create a unique opportunity to develop cheap and fast methods for determining E2. Particularly useful in this field may be the use of biocomposites based on the combination of metal-organic frameworks (MOFs) and enzymes as a biological recognition element. MOFs are an emerging class of nanoporous materials with hybrid organic-inorganic structures. Their attractive properties, such as high surface area, high porosity, flexibility, and good thermal stability, contributed to the fact that MOFs are not only a great scaffold for enzyme immobilization but also can increase their stability and catalytic activity.[2]

This work aimed to develop a novel MOF-based biosensor for determining 17-β-estradiol. The nanocomposite consisting of MOF JUK-2, multi-walled carbon nanotubes (MWCNTs), and gold nanoparticles (AuNPs) was selected as the substrate for the immobilization of the enzyme. The isonicotinate manganese(II) framework (JUK-2) is a two-dimensional MOF with high proton conductivity (above 4×10^{-4} S cm^{-1} in the 70–90% relative humidity range at 25°C) and good stability.[3] Previous research proved that JUK-2 combined with MWCNTs and AuNPs acts as a hybrid material with mixed ion-electron conductivity and excellent electrocatalytic activity.[4] Among tested enzymes, the biosensor based on horseradish peroxidase (HRP) was characterized by the best electrochemical response towards 17-β-estradiol. In the presence of hydrogen peroxide, HRP catalyzes the oxidation of catechol (H_2Q) and 17-β-estradiol (enzyme co-substrates).[5] The electrochemical response of the sensor is proportional to the concentration of H_2Q and inversely proportional to the 17-β-estradiol concentration. At the main stage of the research, the composition of the biocomposite and the procedure of glassy carbon electrode modification were optimized. In order to develop a complete analytical method for the determination of E2, the parameters such as the type, pH of the supporting electrolyte, and H_2Q and H_2O_2 concentrations were selected. Using optimized conditions of analysis, analytical characteristics of the developed biosensor was conducted by determining the sensitivity, linear range, detection limit, and reproducibility. The applicability of the biosensor was verified by E2 determination in urine samples.

Acknowledgments:
This work was funded within the budget of the "Excellence Initiative – Research University" program at the Jagiellonian University in Kraków.

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Sunday, November 5

08:00–09:00		**Breakfast**
09:00–10:40		**Morning session 1** Chairs: C. Branger / M. Cieplak
09:00–09:45	T03	**Karsten Haupt** Synthetic Peptide Antibodies – Principle and Application of Molecularly Imprinted Polymer Nanogels Specific for Protein Epitopes
09:45–10:05	K13	**Peter Lieberzeit** A Closer Look to the Interface: Factors Governing Binding Between Molecularly Imprinted Polymer Thin Films and Their Targets
10:05–10:25	K14	**Petar Kassal** Inkjet Printing of Electrodes for Flexible Electrochemical Sensors
10:25–10:40	SC05	**Alessia Di Fiore** Synthesis and Surface Coating of Molecularly Imprinted Polymer Nanogels Specific for the Heart Failure Biomarker Troponin T
10:40–11:10		**Coffee break**
11:10–13:15		**Morning session 2** Chairs: J. Maciejewska-Komorowska / G. Blanchard
11:10–11:55	T04	**Paweł Kulesza** Low-Temperature Reduction of Electrochemically Inert Molecules: Oxygen, Carbon Dioxide and Nitrogen
11:55–12:15	K15	**Paolo Bollella** Smart Enzyme Conductive Inks for Enzyme-Based Amperometric Biosensors
12:15–12:30	SC06	**Alice Marinangeli** Molecularly Imprinted Nanoparticles and Time-Resolved Fluorescence for the Detection of Protein Contaminants
12:30–12:45	SC07	**Dominik Korol** Chemosensing on Cost-Effective Substrates – a Flexible MIP-Based Chemosensor for Selective Detection of Metronidazole
12:45–13:00	SC08	**Vu Bao Chau Nguyen** MIP-Based Electrochemical Sensors Detecting Antibiotics and Fungicides as Emerging Contaminants in Aqueous Environments
13:00–13:15	SC09	**Christos Galanos** Molecularly Imprinted Polymers for the Selective Recognition and Immobilization of Microorganisms
13:15–14:45		**Group Photo & Lunch**

14:45–16:15		**Afternoon session 1** Chairs: C. Kranz / Ł. Półtorak
14:45–15:05	K16	**Martin Jönsson-Niedziółka** Sequential Microfluidic Device for Point-of-Care Electrochemical Detection of C Reactive Protein Based on a Novel Peptide
15:05–15:25	K17	**Paweł Niedziałkowski** Gold Nanocubes (AuNCs) – Synthesis, Characterization and Selection of a Relevant Surface Modification – for Biosensing Application
15:25–15:45	K18	**Nataliya Stasyuk** Nanozymes as Functional Elements of Biosensors
15:45–16:00	SC10	**Maciej Cieplak** Electroactive Molecularly Imprinted Polymer Nanoparticles for Selective Glyphosate Determination
16:00–16:15	SC11	**Zahra Akbari** AuNP-Enhanced Schiff Base Nanocomposites for Lead (II) Ion Sensing in Seawater
16:15–19:00		**Social event**
19:00–22:00		**Gala dinner**

T03

Synthetic Peptide Antibodies – Principle and Application of Molecularly Imprinted Polymer Nanogels Specific for Protein Epitopes

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Molecularly imprinted polymers (MIPs) are synthetic antibody mimics that specifically recognize molecular targets.[1] They are cross-linked polymers synthesized in the presence of a molecular template, which induces three-dimensional binding sites in the polymer that are complementary to the template in size, shape, and chemical functionality. MIPs against proteins are obtained through a rational approach starting with *in silico* epitope design.[2] Chemically synthesized peptide epitopes can then be used as templates in a solid-phase protocol for MIP synthesis. Fluorescence binding assays, SPR, and solution NMR (saturation transfer difference and WaterLOGSY NMR)[3] are used to demonstrate that the synthetic antibody can recognize and bind its target protein with an affinity and selectivity similar to a biological antibody.

We further demonstrate the potential of MIP nanogels (size ~50 nm) for diagnostics, bioimaging, and therapy, on the example of cell surface biomarker targets,[4,5] as well as soluble biomarkers.[3,6]

Acknowledgments:
K.H. wishes to acknowledge financial support by the National Research Agency of France (ANR) – DynaBio project.

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K13

A Closer Look to the Interface: Factors Governing Binding Between Molecularly Imprinted Polymer Thin Films and Their Targets

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Molecular imprinting into polymers has been around for roughly three decades now. Despite substantial scientific output and appreciable results, there is still only a limited number of cases that see them applied in a commercial manner. Some reasons for that may lie in the polymerization process itself, which – especially in the case of radical polymers – is inherently statistical in nature. This, among others, limits the reproducibility of the sensor layers.[1] On the other hand, MIP nanoparticles resulting from solid-phase synthesis (so-called "MIP nanobodies")[2,3] have overcome those issues: we could demonstrate this for a range of different bioanalytes with mass-sensitive measurements: for instance, MIP nanobodies make it possible to implement competitive assays with quartz crystal microbalances (QCM) for detecting insulin at levels down to 0.8 µM. A similar can be said for vancomycin or an epitope of the NS1 protein of dengue virus. These very appreciable results come at the cost of comparably low yields of functional particles, which, economically speaking, is unproblematic but contradicts the principles of sustainable chemistry.

Fundamentally addressing those issues requires a better understanding of the physicochemical background of both the polymer layers and the surface phenomena taking place during recognition. Especially the first claim seems counterintuitive. However, the so-called AFM PeakForce QNM measurements of non-imprinted cross-linked polystyrene film clearly indicate that it is inhomogeneous regarding mechanical properties, such as adhesion. This demonstrates that mixing styrene and divinyl benzene to achieve 50% cross-linking does not lead to homogeneous materials. On the other hand, we could demonstrate that it is possible to discern the imprints of different bacteria species from each other by Raman microscopy.[4] However, such biological templates are rather complex, comprising a wide range of chemical compounds on their respective surfaces. Therefore, it seems reasonable to utilize microparticles as templates for imprinting thin films because they allow for precisely tuning both size and surface chemistry. First surface imprinting tests further corroborate that the highly cross-linked thin films are indeed rather inhomogeneous regarding their chemical composition. Furthermore, pH-dependent rebinding tests reveal that both the sensitivity and imprinting factor of the system strongly depend on the zeta potentials of the layer and analyte particle. This clearly demonstrates that further understanding the physics and chemistry of the interfacial processes occurring during recognition is of seminal importance.

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K14

Inkjet Printing of Electrodes for Flexible Electrochemical Sensors

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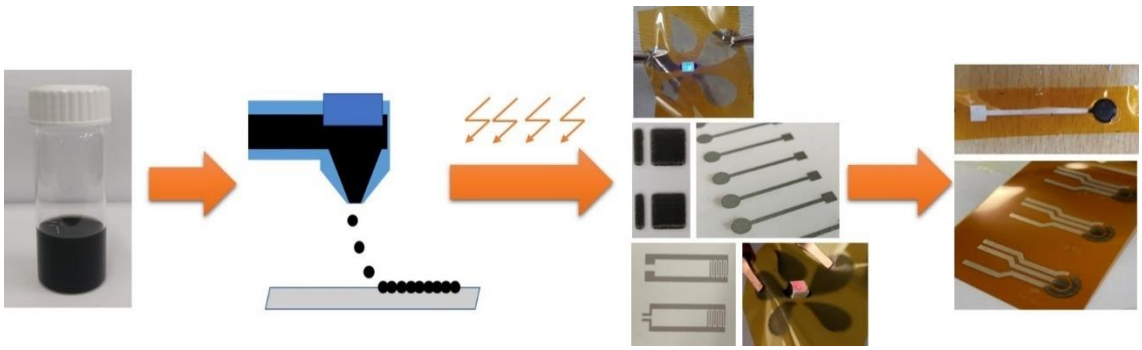
Printed electronics technologies are gaining ground in the development of electrochemical sensors. Specifically, inkjet printing presents a greener, scalable, and cost-effective way of fabricating such devices and moving towards distributed (bio)chemical sensing. A key challenge in the process of inkjet printing of sensors is the formulation of conductive inks with suitable fluid dynamic and surface properties, which are required for adequate jetting, wetting, and adhesion of the ink to the substrate.

In this lecture, the development of flexible electrodes by inkjet printing will be illustrated using two examples: a conductive ink based on silver nanoparticles and a conductive ink based on graphene nanosheets. In the first case, an amphiphilic silver nanoparticle ink was obtained by modifying poly(acrylic acid) capped nanoparticles with 3-morpholynopropylamine (MPA), which provided better adhesion to plastic substrates.[1] The second conductive ink was formulated based on mechanically exfoliated graphene nanosheets stabilized by melamine.[2] Due to its high conductivity, the silver ink was used for printing the electrical contact, and the graphene ink provided an inert surface of the working electrode with a high surface area. Intense pulsed light (IPL), another technology used in printed electronics, was used for electrode processing and sensor development.

Examples will be discussed of how these flexible electrodes were used to develop several key electrochemical sensor components: solid-state Ag/AgCl reference electrodes, solid-contact ammonium-selective electrodes, and voltammetric antibiotic sensors.



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SC05

Synthesis and Surface Coating of Molecularly Imprinted Polymer Nanogels Specific for the Heart Failure Biomarker Troponin T

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Molecularly imprinted polymers (MIPs)[1] are synthetic antibody mimics that specifically recognize molecular targets. They are cross-linked polymers synthesized in the presence of a molecular template, which induces three-dimensional binding sites in the polymer that are complementary to the template in size, shape and chemical functionality.

Here we describe MIPs nanogels directed against the heart failure protein biomarker Troponin T. They were developed through a rational approach starting with *in silico* epitope design by molecular modelling.[2] A chemically synthesized cyclic peptide epitope was then used as a template in a solid-phase protocol for MIP synthesis. Fluorescence binding assays and quartz crystal microbalance were used to demonstrate that the synthetic antibody can recognize and bind specifically its target protein.

We further developed a method based on post-polymerization (making use of residual double bonds in a polymer substrate), and click-chemistry, allowing to coat the MIP nanogels (size ~50 nm) onto the transducer surface.[3]

Acknowledgments:
The authors wish to acknowledge financial support by the National Research Agency of France (ANR) – DynaBio project.

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T04

Low-Temperature Reduction of Electrochemically Inert Molecules: Oxygen, Carbon Dioxide and Nitrogen

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There has been growing interest in environmentally friendly alternative energy sources and methods of formation of fuels and utility chemicals. In this respect, low-temperature electrochemical approaches comprising modern fuel cell technology and electrolytic methods, including conventional and visible-light-induced photoelectrochemical systems, seem to be very promising. With reference to hydrogen-oxygen fuel cells, special attention has been paid to the development of both noble-metal-free and low-platinum-content electrocatalytic materials for efficient oxygen reduction with the ultimate goal of lowering the formation of undesirable H_2O_2 intermediate. The progress in this subject is greatly hindered by the high cost and scarcity of state-of-the-art platinum-based materials, which are regarded as the most effective cathode catalysts. An important strategy addressed here is the hybridization, activation, and stabilization of carbon-supported low-content Pt-catalysts by functionalization with certain nanostructured or substoichiometric metal oxides (e.g., CeO_x or H_xWO_{3-y}), both in simple or mixed forms. Among important issues are not only the improvement of the catalysts performance and ability to decompose undesirable hydrogen peroxide intermediate but also the need to increase their stability.

Regarding the continuously rising levels of atmospheric carbon dioxide, the development of advanced technologies permitting CO_2 utilization is highly desirable. In principle, conventional electrocatalytic and visible-light-induced photoelectrochemical approaches are well-suited for reducing carbon dioxide and possibly generating carbon-based fuels or chemicals. But electroreduction of CO_2 requires large over-potentials and suffers from the competitive hydrogen evolution. To overcome the problem, highly specific and selective catalysts would be required to drive effective conversion (reduction) of carbon dioxide (and water) into fuels, syn-gas, or utility chemicals. Having in mind our recent electrocatalytic results with copper-substituted polytungstates (or polyoxometallate-network-stabilized copper oxo assemblies) and regarding successful utilization of the Cu_2O films over-coated with WO_3 nanowires for both electrochemical and photoelectrochemical reduction of carbon dioxide in near-neutral media, we have pursued research along this line and proposed a hybrid catalytic system composed of copper sites immobilized in tungsten(VI) oxide nanostructures exhibiting improved high selectivity toward CO_2-reduction relative to the competitive hydrogen evolution in acidic medium (0.5 mol dm^{-3} H_2SO_4).

The formation of ammonia is one of the most important chemical synthetic processes. Under industrial conditions, ammonia has primarily been synthesized from nitrogen and hydrogen via the Haber-Bosch process, which requires pressurizing and heating despite the utilization of catalysts. Consequently, developing a low-temperature synthetic methodology is tempting for both practical and fundamental reasons. An ultimate goal for electrochemistry is to generate NH_3 from N_2 at temperatures lower than 100ºC, atmospheric pressure, and using a new generation of catalysts. Currently, most electrochemical approaches to drive N_2-fixation suffer from slow kinetics due to the difficulty of achieving the appropriate adsorption and activation of the dinitrogen molecule, leading to cleavage of the strong triple N≡N bond. Our recent studies clearly demonstrate that coordinatively stabilized iron catalytic sites, e.g., iron-centered heme-type porphyrins or iron phosphide, FeP and Fe_2P phases, have been found to act as efficient catalysts for the formation of NH_3 in alkaline and semi-neutral media.

Developing durable, specific, and reasonably efficient low-cost catalysts for the electroreduction of O_2, CO_2, and O_2 remains a great challenge for electrochemical science and technology. Present trends and future possibilities will be addressed.

K15

Smart Enzyme Conductive Inks for Enzyme-Based Amperometric Biosensors

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Developing disposable and low-cost electrochemical devices for biomedical applications has significantly increased with the diffusion of remote diagnostics. This is probably due to the need for regeneration of the conventional sensor surfaces and the demand for production processes that allow the manufacture of disposable and portable electrochemical devices, promoting the reduction of the volume of samples, *in-situ* detections, and lowering the costs.[1]

Conductive inks are used for the development of disposable electrochemical sensors. They trigger the possibility of building screen- or stencil-printed electrodes with similar efficiency with respect to solid electrodes.[2] In particular, biocompatible inks are formulated and stencil-printed on a flexible support that could be easily integrated within smart devices for the continuous and minimally invasive monitoring of lactate and glucose. First, the conductive ink formulation has been optimized based on electrochemical and rheological measurements implemented within a multivariate analysis model. Afterward, the active carbon electrode was modified with osmium redox polymers (ORPs) to establish an electronic connection with enzymes since neither glucose oxidase (GOx) nor lactate oxidase (LOx) can transfer electrons directly.[3] Finally, both biosensors have been tested in model solution and sweat to determine the analytical figures of merit (e.g., LOD, LOQ, linear range, sensitivity, selectivity, reproducibility, stability, storability, etc.).

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SC06

Molecularly Imprinted Nanoparticles and Time-Resolved Fluorescence for the Detection of Protein Contaminants

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Molecularly imprinted nanoparticles (nanoMIPs) are tailor-made synthetic nanomaterials prepared by a template-assisted synthesis. [1] Recently, nanoMIPs have been exploited as selective and stable recognition elements in sensors due to their biomimetic nature, which makes them alike the biorecognition elements, such as antibodies and enzymes. Recently, a rising interest has been developed in integrating fluorescence into the nanoMIP polymeric network, which appears particularly attractive for the design of optical sensors. [2] Fluorescence is a versatile technique for sensing due to its high sensitivity, low detection limit, real-time response, and simple format.

In the present work, fluorescent nanoMIPs (fluo-nanoMIPs) were designed and used to detect the presence of the model protein human serum albumin (HSA) through time-resolved fluorescence spectroscopy analysis.[3] Fluo-nanoMIPs were synthesized using a total monomer concentration of 0.2% (w/v) HSA as the template and fluorescein *O*-methacrylate as a fluorescent monomer. Fluo-nanoMIPs were physically characterized by dynamic light scattering, and the hydrodynamic size was about 100 nm. Scanning electron microscopy and atomic force microscopy analysis confirmed the dimensions of nanoparticles. The formation of binding cavities suitable to selectively recognize HSA was confirmed by monitoring the fluorescence intensity of fluo-nanoMIPs incubated with increasing concentrations of HSA, while no interaction was reported for competitor proteins. Next, fluo-nanoMIPs, challenged with increasing concentrations of HSA, were tested in solution through time-resolved fluorescence spectroscopy. From these measurements, a decrease in fluorescence lifetime decay was detected, and characteristic saturation binding isotherm was observed with a linear dynamic range of 3.0–83.5 pM and a limit of detection of 1.26 pM. Furthermore, with the idea of developing a portable, compact, and easy-to-use device, we attempted to immobilize the nanoparticles onto a surface through a self-assembling approach. A quartz slide was functionalized with the amino silane APTES, while fluo-nanoMIPs were treated with EDC/NHS (Figure 1).

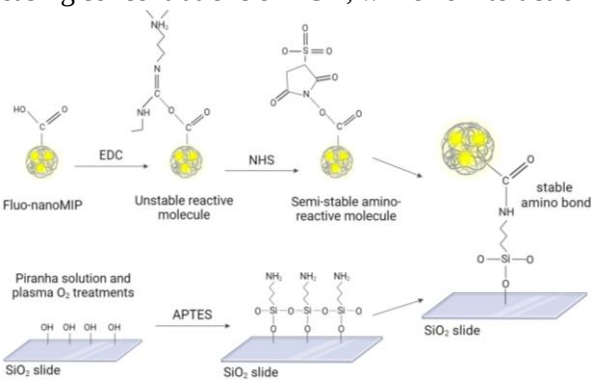

Figure 1. Functionalization of quartz surface.

Our results showed that time-resolved fluorescence of fluo-nanoMIPs specific for recognizing HSA can be used to develop an optical sensing system with a promising ultra-low response that can be exploited to develop diagnostic and environmental sensing systems.

Acknowledgments:
LP and DM thank Strategic Funding Area Covid-19 University of Trento for being awarded the OPTOVIR project. AMB and AM thank MUR for DM 351/2022 PNRR, Missione 4, componente 1.

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SC07

Chemosensing on Cost-Effective Substrates – a Flexible MIP-Based Chemosensor for Selective Detection of Metronidazole

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The increasing amounts of waste discharged into the ecosystem make it necessary to pay particular attention to routine analyses of the chemical composition of sewage, groundwater, and tap water. Especially mass-produced antibiotics, ending up in food products, carry the risk of spreading threatful antibiotic-resistant strains of bacteria. Unfortunately, fabricating chemosensors that selectively detect a given analyte is still expensive, although highly desirable.

The presented research results describe the devising of the chemosensor used to quantify metronidazole (MTZ) – an antibiotic used against *Helicobacter pylori* bacterium, the prevalence of which is estimated at 50% of the human population.[1] The necessity of determining this analyte requires a cost-effective sensor fabrication; hence, our solution was to use carbon paper as a conductive electrode substrate that was then laminated, giving it flexibility. Then, it was coated with a layer of molecularly imprinted polymer (MIP) – the chemical equivalent of biological receptors, whose preparation involves preparing a cross-linked polymer structure with an imprinted template, reversibly connected to the polymer by weak bonds. Cleaving the polymer-template bonds leads to the cavities with the size and shape of template molecules (Figure 1).

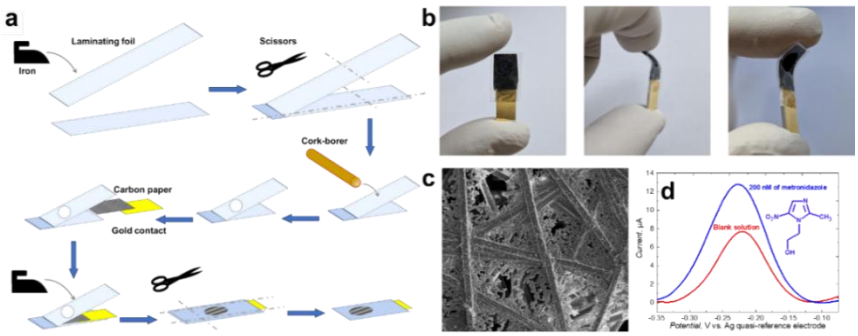

Figure 1. (a) Flowchart showing flexible carbon electrode preparation steps. (b) Optical camera photos of hand-made flexible carbon paper electrode. (c) SEM image of MIP-coated carbon paper. (d) MTZ electrochemical determination[2].

The extracted MIP film over the electrode surface captures analyte molecules like antibodies that capture biomolecules. However, the capabilities of polymers overcome those of enzymes due to better thermal stability and chemical resistance with comparable limits of detection.[3]

A laminated carbon paper electrode was electrochemically coated with pyrrole-based polymers with an imprinted antibiotic, resulting in a chemosensor enabling the analyte determination even in the sub-nanomolar concentration range, showing selectivity towards other biomolecules, confirmed with differential pulse voltammetry (DPV) technique using a redox probe as a signal transducer. It has also been proven that the prepared sensor enables the determination of the analyte in real samples – in a suitably diluted honey solution.

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SC08

MIP-Based Electrochemical Sensors Detecting Antibiotics and Fungicides as Emerging Contaminants in Aqueous Environments

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The increasing problem of environmental pollution poses a significant threat to both public health and the balance of ecosystems. One of the main contributors to this issue is the spread of agricultural fungicides and antibiotic pollutants in water bodies, which has become a major concern.[1,2] Consequently, there is an urgent need to develop selective and reliable detection methods to monitor these pollutants in aqueous environments, ensuring environmental safety and public health.

This study addresses these challenges by developing electrochemical sensors utilising molecularly imprinted polymers (MIPs) as the recognition elements. These innovative sensors are designed to specifically recognise and measure azoxystrobin – a broad-spectrum fungicide in agriculture and macrolides – antibiotics commonly found in aqueous ecosystems.[3] By capitalising on the unique selectivity of MIPs, these sensors provide improved sensitivity and precision that allows them to accurately detect and trace the amounts of these harmful substances in water systems.

For the detection of azoxystrobin, the azoxystrobin-selective MIP was synthesised on the working electrode of a thin metal electrode system. Aniline and *meta*-phenylenediamine (mPD) were used as functional monomers, offering superior binding energy with azoxystrobin and facilitating the formation of a tailored three-dimensional polymeric network. The optimised sensor demonstrated good selectivity with a low limit of detection (LOD) of 2.0 nM and a limit of quantification (LOQ) of 6.8 nM.

For the detection of antibiotic macrolides, an electrochemical sensor was designed based on a macrolide-selective MIP film synthesised on a screen-printed electrode. The MIP film was prepared by electrochemical polymerization of 3-aminophenyl boronic acid and mPD as dual-functional monomers in the presence of erythromycin as a template. The optimised sensor exhibited five times more specific adsorption for macrolides, including erythromycin, clarithromycin, and azithromycin, than a reference sensor modified with a non-imprinted polymer (NIP). The sensor achieved a low LOD and LOQ in the range of 1.1–1.7 nM and 3.7–5.5 nM, respectively, with impressive selectivity in PBS solution and tap water samples.

The preliminary results demonstrate distinct MIP-based electrochemical sensors achieved high sensitivity and good selectivity while detecting antibiotic macrolides and fungicide azoxystrobin within water sources. This work showcases the potential of MIP-based electrochemical sensors as versatile tools for the on-site detection of diverse environmental contaminants, contributing to water quality monitoring and risk assessment.

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SC09

Molecularly Imprinted Polymers for the Selective Recognition and Immobilization of Microorganisms

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Molecularly imprinted polymers (MIPs) are receptor-like biomimetic materials. They are cross-linked polymers synthesized in the presence of a molecular template, which induces three-dimensional binding sites in the polymer that are complementary to the template in size, shape, and position of chemical groups.

In the present work, they were used to recognize and immobilize photosynthetic bacteria on polymeric scaffolds. Due to the challenges of imprinting whole bacteria,[1] cell membrane proteins were more reasonable candidates for cell recognition. Thus, the Slr1270 protein from the cyanobacterium *Synechocystis sp.* PCC 6803 was chosen as the target protein for imprinting using protein structure databanks and bioinformatics tools.[2] Two epitope sequences were selected and validated by an *in silico* rational approach, and then the peptide template was chemically synthesized. MIPs targeting the Slr1270 peptide epitopes were then synthesized by a solid-phase approach. *N*-propylacrylamide (NPAm) was incorporated as the main monomer into the polymerization mixture to generate thermoresponsive MIPs that feature a lower critical solution temperature (LCST) around 25ºC. The MIP-NGs were then characterized using dynamic light scattering (DLS) and scanning electron microscopy (SEM). The resulting MIPs showed the ability to recognize and bind their template epitope peptide and the whole bacterium, as shown by fluorescent equilibrium binding assays, flow cytometry, fluorescence microscopy, and SEM.

Acknowledgement:
The authors wish to acknowledge financial support by European Union FET-Open FuturoLEAF project.

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K16

Sequential Microfluidic Device for Point-of-Care Electrochemical Detection of C-Reactive Protein Based on a Novel Peptide

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Point-of-care testing (POCT) devices are currently available and have substantially expanded the ability to detect various important biomarkers and diseases, such as SAR-CoV-2, cancer, diabetes, and cardiovascular diseases (CVDs) since they provide features in terms of ease of use, portability, rapid response, and low-cost platform.[1] However, the multistep reagent manipulation still impedes the performance of the device for end users. Herein, we report the use of a microfluidic device that integrates dual flow behavior (fast-flow/delayed) within a single device to determine the risk of CVDs. C-reactive protein (CRP) was used as the model CVD biomarker in this work. Capillary-driven microfluidics was applied to enable sequential reagent delivery. The microfluidic device consists of five main components: a sample and buffer inlet zone, a fast-flow channel adapted from a previous report by Jang et al.[2] and Boonkaew et al.,[3] a time-delayed channel to obtain fully automated electrochemical detection, a screen-printed electrode, and the passive pump paper to serve as a waste reservoir and control the fluid flow of the device. To assemble the device, transparent PET film and double-sided adhesive tape (DSA) were integrated in a sandwiched layer manner. Once the running buffer is loaded at the inlet zone, the automated washing of unbound antigens and transporting of the redox reagent in a sequential platform are acquired (the analysis time can be completed within 15 min). The concentration of CRP in samples was quantified using chronoamperometry (CA). Generally, the measurement of CRP is performed by antibodies through enzyme-linked immunosorbent assay (ELISA). However, the storage stability and affinity of antibodies are still an issue in manufacturing. To address this limitation, the P3-CRP peptide was prepared using phase display technology and integrated as a new bioreceptor for CRP detection. The performances using both antibody and P3-CRP peptide were examined and discussed. The detection limit of the proposed device was as low as 47 pg mL^{-1} with a wide linear range (5 orders of magnitude). To confirm the applicability, this device was tested in serum and whole blood samples and gave a satisfactory result. The developed microfluidic device will have a significant impact in the field of low-cost, easy-to-use, and point-of-need diagnostics, and this impact will be broadened and expanded to other biosensing applications.

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K17

Gold Nanocubes (AuNCs) – Synthesis, Characterization and Selection of a Relevant Surface Modification – for Biosensing Application

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Nanomaterials are now of great interest as they exhibit significantly different behaviour from those presented by bulk materials. The modification of optical, electrochemical, and magnetic properties through the use of specific nanomaterials results in their increasing use in many fields, including molecular recognition and the development of new optical and electrochemical sensors and biosensors.

Gold nanoparticles (AuNPs) are one of the most commonly studied nanomaterials due to their extraordinary properties, such as biocompatibility, and optical and electrical enhancement, mainly depending on their particle dimensions, geometry, and molecular structures. From the perspective of biosensor development, an additional advantage of applying gold nanoparticles is the ability for their further modification to obtain more complex materials. The surface of gold nanoparticles can be functionalised by several methods, mainly by forming self-assembled monolayers with thiol derivatives or in a reaction with other compounds. Nevertheless, the selectivity and sensitivity of the modified electrodes are greatly influenced by the type of nanoparticles used in the first stage of electrode modification. These affect the surface electron transfer ability to promote the catalytic process. Therefore, it is extremely important to select the most appropriate nanoparticles with an electrochemical activity directly related to their particle size, structure, and crystallographic orientation. There are a lot of synthesis methods for obtaining gold nanoparticles characterised by different shapes and regularity in structure, such as cubes, rods, plates, or pyramids. For this reason, gold nanocubes (AuNCs) are of great interest in creating new electrochemical biosensors due to their regularly shaped and three-dimensional structure. AuNCs also exhibit higher chemical stability in comparison to standard gold nanoparticles. Interest in utilising AuNCs for electrode modification results from the fact that each cube has the same shape and geometry, which increases the number of active sites on the electrode surface. Additionally, each cube can either form regular shapes on the surface or be randomly distributed, resulting in a greater possibility of their functionalisation.[1]

The presented research results will focus on describing the methods of AuNCs preparation, their properties, and characterisation. The effect of the presence of AuNCs at the surface of three different types of electrodes (Au, GC, ITO) on their electrochemical activity will be discussed. Furthermore, the selected methods of electrode modification using gold nanoparticles for biosensing applications will be reviewed.

Acknowledgments:
This work was supported by the National Science Centre under Project 2020/37/B/ST7/03262.

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K18

Nanozymes as Functional Elements of Biosensors

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The ever-increasing need for early diagnosis of many diseases, improvement of environmental protection, and control of the quality of food products and drinking water requires a broad practical use of highly sensitive, selective, fast, and economical analytical methods. Among various approaches, a special role is assigned to analytical biotechnology – a branch of science that uses the principles of biomolecular recognition to identify and quantitatively determine practically important analytes. Modern analytical biotechnology uses very selective biorecognition systems created by nature: enzyme-substrate (cofactor, effector-inhibitor), hormone-receptor, antigen-antibody, complementary interactions of nucleic acids, complexes involved in regulating gene expression, and signaling cascade complexes.[1,2] In recent years, artificial biomimetics – aptamers, abzymes, nanozymes – have also been used as bioanalytical tools.[3]

Nanozymes (NZs), as stable, cost-effective mimics of natural enzymes, may be promising catalysts in food and environmental biotechnology, biosensorics, alternative energy, and medicine.[4] Enzyme-like NZs, including metallic nanocomposites, are promising catalysts for biosensing applications. Three main classes of NZs are known: peroxidase-like, oxidase-like, and antioxidant NZs. Artificial peroxidase being able to utilize as a substrate hydrogen peroxide, the final product of oxidase-catalyzed splitting of different practically important analytes, may be a promising hydrogen peroxide-selective chemosensing element, coupled with a relevant oxidase in the biosensing layer.[5]

The aim of the current research is to construct novel NZs-based biosensors coupled with microbial enzymes, promising for medical diagnostics and food analysis, using NZs as peroxidase, reductase mimetic catalysts, or nanochelators for small molecules. The constructed NZs-based novel biosensors have been applied to detect L-arginine, creatinine, methyl amine, ethanol, and glucose. A high correlation was demonstrated for the contents of the target analytes, estimated by the developed biosensors and the reference enzymatic methods. The proposed biosensor approaches, being sensitive, economical, and suitable for routine and micro-volume formats, can be used in clinical diagnostics to detect the target analytes.

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SC10

Electroactive Molecularly Imprinted Polymer Nanoparticles for Selective Glyphosate Determination

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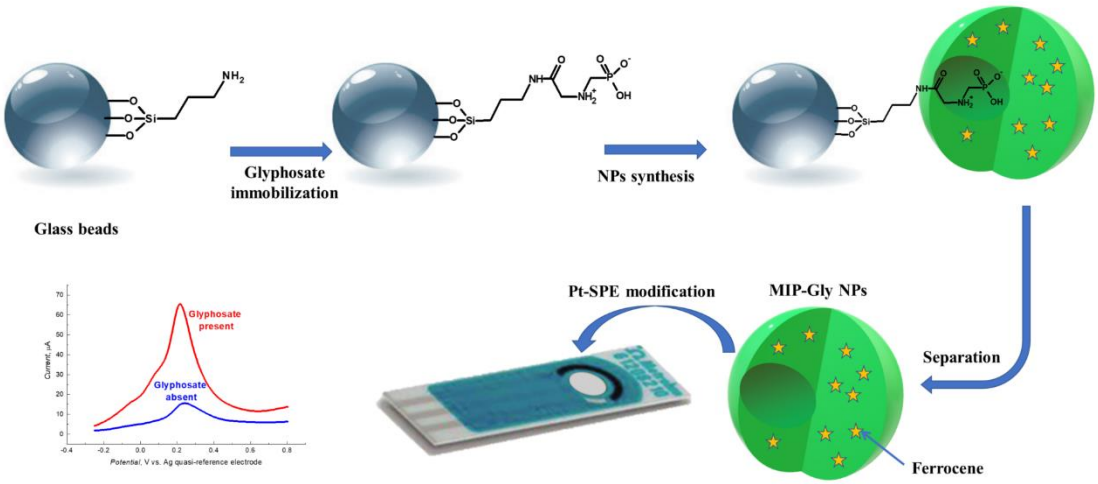
Redox-active molecularly imprinted polymer nanoparticles selective for glyphosate, MIP-Gly NPs, were devised, synthesized, and subsequently integrated onto platinum screen-printed electrodes (Pt-SPEs) to fabricate a chemosensor for selective determination of glyphosate (Gly) without the need for redox probe presence in the test solution (Scheme 1).[1] That was because ferrocenylmethyl methacrylate was added to the polymerization mixtures during the NPs synthesis so that the resulting MIP-Gly NPs contained covalently immobilized ferrocenyl moieties as the self-reporting redox component, conferring the NPs with electroactive properties.



Scheme 1. The flowchart of a general MIP-Gly NPs synthesis and a selective Gly-chemosensor fabrication.

The Pt-SPEs modified with MIP-Gly NPs were characterized with differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS). Changes in the DPV peak originating from the electro-oxidation of the ferrocenyl moiety in these MIP-Gly NPs served as the analytical signal. The DPV limit of detection and the linear dynamic concentration range for Gly were 3.7 pM and 25–500 pM, respectively. Moreover, the selectivity of the fabricated chemosensor was sufficiently high to determine Gly in spiked river water samples successfully.

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SC11

AuNP-Enhanced Schiff Base Nanocomposites for Lead (II) Ion Sensing in Seawater

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Heavy metal pollution stands as a significant environmental peril, casting detrimental impacts on ecosystems and human well-being. Lead (Pb), due to its persistent toxicity and propensity for bioaccumulation, emerges as a particularly concerning heavy metal.[1] The surveillance and detection of lead ions (Pb^{2+}) within aquatic realms encompassing seawater environments hold paramount importance in safeguarding the environment and public health. Amongst the array of techniques, electrochemical sensors have emerged as potent instruments, delivering sensitive and selective Pb^{2+} detection, with added benefits including swift responsiveness, portability, economic viability, and the ability for real-time monitoring.

In recent times, Schiff base ligands have garnered considerable attention as agents in crafting electrochemical sensors dedicated to heavy metal detection, including Pb^{2+}.[2] These organic compounds, derived from the condensation of primary amines and carbonyl compounds, exhibit diverse chemical structures endowed with customizable properties. Their remarkable specificity and sensitivity towards diverse metal ions render them prime candidates for conceiving electrochemical sensors targeting heavy metals.

The remarkable characteristics of Schiff base ligands originate from their capability to establish stable complexes through coordination bonds with metal ions.[3] The incorporation of Schiff base ligands (L) into the architecture of electrochemical sensor platforms enables the attainment of elevated sensitivity and selectivity for detecting heavy metals within complex sample matrices, including seawater.

Electrochemical sensors built upon Schiff base ligands employ varied transduction mechanisms, spanning amperometry, potentiometry, and voltammetry, to translate metal-ligand interactions into quantifiable electrical signals. These signals bear a direct correlation to the concentration of the sought-after metal ion, thereby enabling precise quantification of heavy metal contaminants.

This study endeavors to exemplify the application of a pioneering Schiff base ligand in an electrochemical sensor tailored for Pb^{2+} detection in a basic pH, mimicking the typical pH of seawater, akin to seawater conditions. The study encompasses a comprehensive exploration of design principles, synthetic strategies, and characterization methodologies entailed in the synthesis of the Schiff base ligand. Furthermore, the study delves into the evaluation of a screen-printed carbon electrode, modified with the synthesized tetradentate Schiff base ligand (L/SPCE), as well as with gold nanoparticles-tetradentate Schiff base ligand (AuNPs-L/SPCE), for the accurate determination of minute quantities of Pb(II) utilizing square wave anodic stripping voltammetry (SWASV).

Acknowledgments:
This work has been partially funded by the European Union (NextGeneration EU) through the MUR-PNRR project SAMOTHRACE (ECS00000022).

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Monday, November 6

08:00–09:00		**Breakfast**
09:00–10:40		**Morning session 1** Chairs: M. Wiloch / F. Marken
09:00–09:45	T05	**Gary Blanchard** The Piezoelectric Effect in Ionic Liquids. Mechanistic Insights and Sensing Applications
09:45–10:05	K19	**Catherine Branger** Towards Novel Sensing Receptors Based on Modified Gold Electrodes by Active Molecularly Imprinted Polymers
10:05–10:25	K20	**Paweł Krysiński** Iron Oxide Superparamagnetic Nanoparticles for the Adsorption and Photocatalytic Degradation of Pharmaceutics. Tetracycline Case
10:25–10:40	SC12	**Juliana Cancino-Bernardi** Cell Membranes Used as Biorecognition Element to Impedimetric Biosensing
10:40–11:10		**Coffee break**
11:10–12:55		**Morning session 2** Chairs: S. Grecchi / M. Jönsson-Niedziółka
11:10–11:30	K21	**Ilaria Palchetti** Microfluidic Procedure for the Electrochemical Biosensing of Isothermally-Amplified DNA
11:30–11:50	K22	**Sabine Kuss** Disease Detection at the Microscale – Cytochrome C Oxidase Deficiency Quantification in Human Fibroblasts
11:50–12:10	K23	**Jacek Ryl** Multivariate Data Analysis of Multisine Impedimetric Fingerprints in Electroanalysis of Biochemical Compounds
12:10–12:25	SC13	**Krzysztof Noworyta** Biphenol Selective Electrosynthesis on the Molecularly Imprinted Polymer-Coated Electrodes
12:25–12:40	SC14	**Parastoo Vahdatiyekta** Synthesis and Application of BTMDs in E-Tongue for Detecting Homovanillic Acid: a Potential Breast Cancer Biomarker
12:40–12:55	SC15	**Alexandra Canciu** Electrochemical Aptamer-Based Sensors for the Label-Free Detection of Pathogen Bacteria
13:15–14:45		**Lunch**

14:45–16:20		**Afternoon session 1** Chairs: S. Kuss / K. Noworyta
14:45–15:05	K24	**Wojciech Nogala** Analysis of Heterogeneous Hydrogen Evolution with Scanning Electrochemical Microscopy
15:05–15:25	K25	**Christine Kranz** Surface Modification via Scanning Electrochemical Probe Microscopy (SEPM): from Molecular Catalyst Arrays to Antimicrobial Surfaces
15:25–15:45	K26	**Jean-Marc Noël** Unraveling the Mechanism of Aryldiazonium Reduction: Evidence and Quantitative Analysis of Reactive Intermediates and Byproducts
15:45–16:05	K27	**Vitali Syritski** Electrochemical Sensing of Clinically Relevant Proteins by Molecularly Imprinted Polymer-Modified Electrodes
16:05–16:20	SC16	**ST Balamurugan Thangaraj** Electroanalytical Screening of Clozapine (Date and Rape Drug) in Soft and Hard Drinks at Electrified Liquid-Liquid Interfaces
16:30–17:00		**Coffee break**
17:00–18:15		**Afternoon session 2** Chairs: J. Kochana / L. Jeuken
17:00–17:20	K28	**Bartłomiej Graczykowski** Mechanical and Thermal Engineering of Functional Nanomembranes
17:20–17:40	K29	**Emilia Witkowska-Nery** Simple Systems for Electrochemical Ion Sensing
17:40–18:00	K30	**Łukasz Półtorak** Drugs, Membranes, 3D Printing and Sensing at Electrified Soft Junctions
18:00–18:15	SC17	**Julia Maciejewska-Komorowska** Transfer of Sulfate Ions Between Immiscible Liquids at the Three-Phase Junction Using a Novel Compound
19:00–20:00		**Dinner**
21:00–3:00		**Disco**

T05

The Piezoelectric Effect in Ionic Liquids. Mechanistic Insights and Sensing Applications

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The piezoelectric effect is well established in solid-state materials that possess a center of inversion and in a variety of composite materials. The piezoelectric effect has found extremely broad utility in sensing, with the ubiquitous deployment of accelerometers and as actuators in STM and AFM instruments, for example. Until our recent report,[1] the piezoelectric effect was not known to exist in liquids. Our work with ionic liquids has demonstrated both the direct and converse piezoelectric effects. The existing theory for the piezoelectric effect in solids couples Hooke's law and the displacement of charge in a dielectric, both of which are not easily reconciled with the physical properties of ionic liquids. Through an examination of several ionic liquids, we have determined that the application of compressive force to the ionic liquid causes a liquid-to-solid phase transition, and it is the solid form of the ionic liquid that is responsible for the piezoelectric response. Despite several apparent violations of the assumptions underlying the current model for piezoelectric behavior, the model predicts experimental behavior effectively, including the linear (Pockels effect) and second-order nonlinear optical (SHG) response of piezoelectrics. We have found these optical properties in ionic liquids.

With the ability of ionic liquids to exhibit the piezoelectric effect, we are able to consider novel applications, including spatially-resolved sensing and the direct quantitation of angular acceleration. Both of these applications have direct relevance to current needs in biomedical sensing.

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K19

Towards Novel Sensing Receptors Based on Modified Gold Electrodes by Active Molecularly Imprinted Polymers

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The conception of molecularly imprinted polymers (MIPs) is based on a biomimetic approach to reproduce the specific interactions between antibodies and antigens. Whereas antibodies are usually expensive to prepare and sensitive to their environment, producing MIPs is more affordable and stable in various conditions. The recognition properties of MIPs originate from specific interactions between at least one functional monomer and the target molecule. Using a redox probe as a functional monomer, we introduced the concept of electrochemical MIPs (e-MIPs).[1–3] These smart MIPs can act as specific receptors in sensors and transduce the recognition of the target molecule in an electrochemical signal.

In this talk, we will present our last advances in designing modified gold electrodes based on e-MIPs for detecting polycyclic aromatic hydrocarbons (PAHs) (Figure 1).

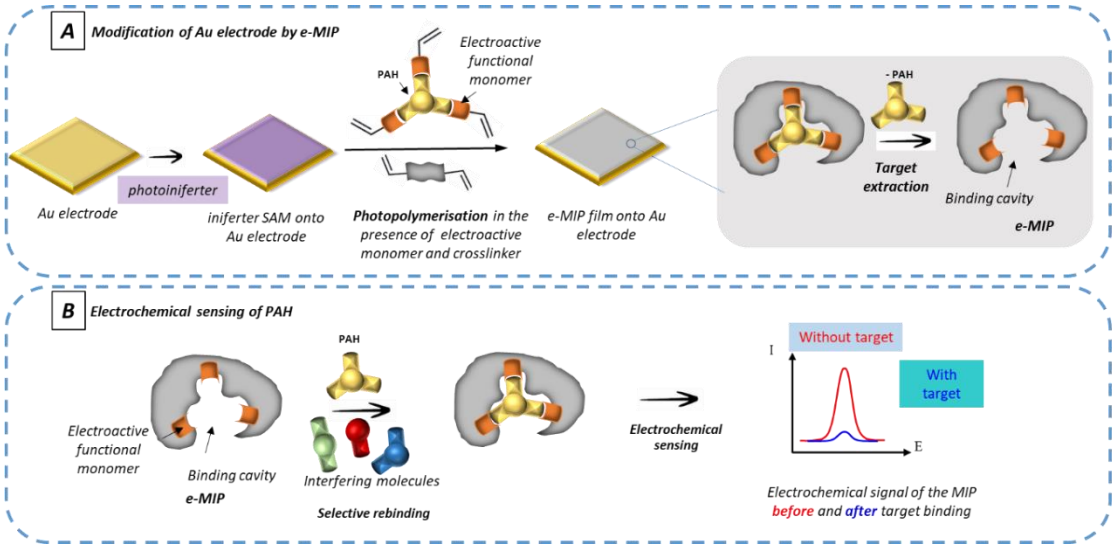

Figure 1. Schematic representation of the modification of gold electrodes by e-MIPs and their use for electrochemical detection of PAH.

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K20

Iron Oxide Superparamagnetic Nanoparticles for the Adsorption and Photocatalytic Degradation of Pharmaceutics. Tetracycline Case

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Antibiotics were developed to limit the mortality rate and boost human and animal immune systems, which have been negatively affected by the invasion of different bacteria's infection. Meanwhile, the uncontrolled disposal of antibiotics into the environment through the industrial, hospital, household, and livestock wastewater has compromised their disease-fighting ability and made them detrimental to the environment, particularly to human health. Therefore, the challenges associated with the uncontrolled presence of antibiotics, such as tetracycline, in the environment have necessitated their removal through different techniques. Tetracycline is hard to degrade in living organisms and can even be converted to more toxic substances. Given this, we synthesized iron oxide nanoparticles with good magnetization (70 emu g^{-1}) and 15 nm particle size for the adsorption and photocatalytic degradation of tetracycline. Characterization of the synthesized iron oxide nanoparticle revealed a bandgap of 1.83 eV and an isoelectric point at pH = 6.8. The results also showed that the pH of the solution does not directly influence the adsorption of tetracycline. The adsorption isotherm was consistent with the model proposed by Langmuir, having a 97 mg g^{-1} adsorption capacity. The mechanisms of adsorption were proposed to be hydrogen bonding and *n*-π interactions. Photocatalytic degradation studies showed that approximately 40% of tetracycline degraded within 60 min of irradiation with UV-Vis light. The kinetics of photodegradation of tetracycline followed the pseudo-first-order mechanism, proceeding through hydroxyl radicals generated under illumination. Moreover, the photogenerated hydrogen peroxide could lead to heterogeneous photo-Fenton processes on the surface of iron oxide nanoparticles, additionally generating hydroxyl and hydroperoxyl radicals and facilitating the photodegradation of tetracycline. Combined with the superparamagnetic behavior, the adsorption capacity, and photocatalytic properties, these nanoparticles proved to be advantageous for the magnetic extraction of tetracycline from wastewater. The reusability and regeneration through thermal treatment were evaluated and revealed that up to several adsorption/photocatalytic degradation cycles of the same nanoparticle batch can be carried out with little loss of efficiency.

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SC12

Cell Membranes Used as Biorecognition Element to Impedimetric Biosensing

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Biomimicking nanoparticles with cell membranes is one of the most innovative approaches to enhance performance, selectivity, and functionality for biomedical applications.[1,2] The cell membrane coating provides several advantages, such as enhanced biocompatibility, improved stability, and specific targeting capabilities due to the inherited properties of the source cells.[3] These advantages can be transferred to the biosensing scenario. For example, to improve the specificity and selectivity of SARS-CoV-2 biosensors, the angiotensin-converting enzyme 2 (ACE-2) transmembrane receptor, which is overexpressed in respiratory model cells, was used as a biorecognition element. In this new SARS-CoV-2 detection platform, cellular membranes from VeroCCL81 (mVero) and Calu-3 (mCalu) cells (which overexpress the ACE-2 transmembrane receptors) were extracted and immobilized as vesicles on an indium tin oxide electrode (ITO). Electrochemical impedance spectroscopy was used to optimize the performance of the developed devices for SARS-CoV-2 detection. The membrane biosensors showed the limit of detection of 10.0 pg mL^{-1} and 7.25 pg mL^{-1}, and the limit of quantification of 30.4 pg mL^{-1} and 21.9 pg mL^{-1} were achieved with satisfactory accuracy for ITO-APTES-mVero and ITO-APTES-mCalu, respectively. Selectivity studies revealed that this platform was able to differentiate the target spike proteins from NS1 proteins from dengue and Zika viruses. Using biorecognition between cell membranes that express the ACE-2 receptors and the virus spike protein may be a new and efficient way to diagnose SARS-CoV-2, especially in terms of the cost of production and isolation, compared to other targets.

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K21

Microfluidic Procedure for the Electrochemical Biosensing of Isothermally-Amplified DNA

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Many bioanalytical techniques have been developed to detect target DNA fragments in biological and environmental samples, but most of them require a significant amount of time, attention, and work from expert personnel to thoroughly follow the analysis and obtain reliable results.

In this work, a new microfluidic system was exploited to design an easily-produced chip-based architecture that implements all the steps required for a full DNA assay, requiring limited manual work and small sample volumes. Superparamagnetic microbeads functionalized with a DNA capture probe are used as the solid phase of the assay. These microbeads are first injected into the microchannel of a flow-based chip, where a removable magnet is used to retain the beads in position. Then, a microfluidic flow, controlled by a peristaltic pump, will put them in contact with a signaling probe, used to generate a measurable electrochemical signal, and the sample containing the DNA target in analysis. Hybridization occurs, resulting in a sandwich-like conjugate coupled to an enzyme capable of converting a proper substrate into an electroactive moiety, thus providing electrochemical signal amplification.

Optimizations were introduced by identifying the most effective workflow, e.g., washing steps, incubation times, and the single flow rates of each step to increase efficiency and sensitivity. In this way, it was possible to considerably decrease the volume of reagents and the overall experimental runtime. The system proved efficient in the proof-of-concept analysis of short DNA strands, with detection limits in the picomolar range, using only a few microliters of the target DNA sample and presenting results in less than one hour. Implementing isothermal amplification techniques inside the microfluidic chip to enhance the platform sensitivity is also expected. The platform achieved good limits of detections with synthetic genes and was able to detect down to ≥500-fold diluted amplification products of selected genes, thus enabling numerous end-point analyses with a single amplification reaction.

Acknowledgments:
Financial support from Regione Toscana Bando Salute 2018 (Research project CUP n. D78D20000870002) is acknowledged.

K22

Disease Detection at the Microscale – Cytochrome C Oxidase Deficiency Quantification in Human Fibroblasts

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This presentation illustrates the ability of scanning electrochemical microscopy (SECM) to detect and quantify diseases in human cells. Cytochrome c oxidase deficiency (COXD) is an inherited disorder characterized by the absence or mutation in the genes encoding the cytochrome c oxidase protein (COX). COX deficiency results in severe muscle weakness, heart, liver, and kidney disorders, as well as brain damage in infants and adolescents, leading to death in many cases. With no cure for this disorder, finding an efficient, inexpensive, and early means of diagnosis is essential to minimize symptoms and long-term disabilities. Muscle biopsy, the traditional detection method, is invasive, expensive, and time-consuming. This study demonstrates the applicability of SECM to quantify COX activity in living human fibroblast cells. Taking advantage of the interaction between the redox mediator *N*,*N*,*N*',*N*'-tetramethyl-*para*-phenylene-diamine, and COX, the enzymatic activity was successfully quantified by monitoring current changes using a platinum microelectrode and determining the apparent heterogeneous rate constant k_0 using numerical modeling. This study provides a foundation for developing a new diagnostic method for detecting COXD in infants, which has the potential to increase treatment effectiveness and improve the quality of life of affected individuals.

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K23

Multivariate Data Analysis of Multisine Impedimetric Fingerprints in Electroanalysis of Biochemical Compounds

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Two primary concerns for biosensors operating in real environments are electrode fouling and highly complex, hard-to-scale electrode nanoarchitectures. The following talk will be dedicated to introducing a novel approach to the modus operandi of electrochemical biosensors designed to mitigate these issues. By implementing a real-time dynamic electrochemical impedance spectroscopy (DEIS) carried out at various electrode potentials, we obtain full impedance characteristics constituting an explicit fingerprint of the macromolecular interactions.

Recently, DEIS allowed us to obtain the unique fingerprint of the electric parameter changes specific to studied macromolecules (such as DNA strings, viral proteins, RNA polymerase, and enzymes).[1–4] Multivariate data analysis processes large amounts of generated impedimetric data and brings information on analyte-sensitive conditions (DC polarization, AC amplitude, frequency range, etc.), which can be done just by using the raw data by the singular-value decomposition (SVD) to support the sensing mechanisms. The proposed approach neglects some reproducibility issues induced by non-specific adsorption and fouling. It reveals the measurement conditions that offer the highest variation of studied parameters upon specific analyte adsorption.

For the first time, we combined DEIS, SVD, and partial least square discriminant analysis (PLS-DA) to provide specific identification of the analyte from raw impedimetric data. As a proof-of-concept, we have selected the identification of uropathogenic *E. coli* in real human urine by the RNA polymerase (RNAP) interaction with an aptamer-based biosensor. The biosensor is responsive not only to binding moieties but also to coulombic interactions between the analyte and self-organized, drop-casted, receptor-functionalized Au nanocube (AuNC) patterns, used to enhance signal strength.[4,5] This novel strategy revealed uropathogenic *E. coli* strain No. 57 limit of detection of 10 CFU mL^{-1} in real human urine, with the result available in just two minutes. A simple glassy carbon electrode was used with drop-casted AuNCs prior to the experiment without using any anti-fouling strategies. The proposed methodology is easy to transfer to different analytes.

Acknowledgments:
The authors acknowledge the financial support of these studies by the National Science Centre (Republic of Poland) under project 2020/37/B/ST7/03262.

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SC13

Biphenol Selective Electrosynthesis on the Molecularly Imprinted Polymer-Coated Electrodes

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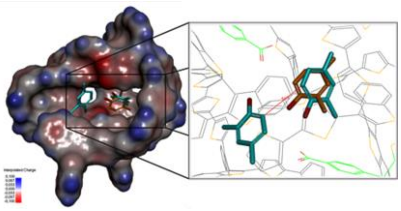
Herein, we report on applying molecularly imprinted polymer (MIP) film for selective electrochemical phenol-to-biphenol conversion.

Molecular imprinting is attractive as it allows the fabricating of artificial receptors exhibiting highly shape-selective interaction with target compounds, making them suitable for, e.g., sensors, separation, and catalytic applications.[1] The MIPs advantages include their high stability under various conditions, facile preparation, and manipulation. An exciting field of MIP application, still underdeveloped, is catalysis. Selective synthesis/catalysis at MIPs relies on imprinting either substrate to enhance its concentration near the reaction site or the product to promote enzyme-like shape-selective catalysis.[2] Moreover, the reaction intermediate can be imprinted to drive the reaction via the desired route.



Scheme 1. Molecular dynamics simulated positions in the MIP molecular cavity of one $DMPh^{\bullet+}$ radical cation molecule substrate (orange) or two $DMPh^{\bullet+}$ radical cation molecules (turquoise).

We developed a synthetic procedure of the 2,4-dimethylphenol (DMPh) substrate direct electro-oxidation to the C–C coupled 3,3',5,5'-tetramethyl-2,2'-biphenol (TMBh) product using a MIP film-coated electrode. To this end, we have used the TMBh product as the template for imprinting. We have performed a series of DFT calculations of template-(functional monomer) interactions using various functional monomers to select the one most appropriate. Calculations indicated that deprotonated carboxyl-containing thiophene-based functional monomer formed a pre-polymerization complex at a template-to-monomer molar ratio of 1:2 sufficiently strong to survive the electropolymerization. We followed pre-polymerization complex formation using UV-Vis and FT-IR spectroscopy. Next, we prepared the MIP film by electropolymerization of the pre-polymerization complex and then characterized it electrochemically and spectroscopically. The film morphology and nanomechanical properties were unraveled using AFM. Afterward, we applied the MIP film-coated electrode for the DMPh electro-oxidation. Both MIP film thickness and electrosynthesis parameters significantly affected this electrosynthesis yield and selectivity. The TMBh electrosynthesis at the MIP film-coated electrode was significantly more selective than over the bare and control non-imprinted polymer (NIP) film-coated electrode. We have used computer simulations of imprinted cavity interaction with the substrate molecules to understand this electrosynthesis more deeply.

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SC14

Synthesis and Application of BTMDs in E-Tongue for Detecting Homovanillic Acid: a Potential Breast Cancer Biomarker

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The global rise in cancer cases emphasizes the pressing need for innovative, affordable, and swift diagnostic methods. Utilizing urine as a diagnostic medium offers a non-invasive and efficient method for early detection. This approach facilitates prompt interventions, leading to improved patient outcomes, including reduced treatment costs, shorter recovery times, minimized complications, and enhanced quality of life. Among the various techniques employed to analyze and track alterations in these samples, the electronic tongue (e-tongue) or electronic nose (e-nose) stands out. These devices harness the advantages of the diversity of sensing materials and techniques, enhancing the precision and reliability of the diagnostic process.

This study presents the synthesis of *N*,*N*'-bis(2-thienylmethylene)-1,*N*''-benzenediamine (BTMD) isomers and their application in the construction of an e-tongue, specifically designed for the detection of metabolite biomarkers in urine. Three Schiff-base compounds, *ortho*-BTMD, *meta*-BTMD, and *para*-BTMD with the formula of ($C_{16}H_{12}N_2S_2$), were synthesized by the reaction of 2-thiophenecarboxaldehyde with *ortho*-, *meta*-, and *para*-phenylenediamine respectively with the molar ratio of 2:1. The structure of BTMDs with the molecular mass of ~296 g mol^{-1} were confirmed by mass spectrometry and NMR, and further characterized by XPS, Raman and IR spectroscopy, UV-Vis, and cyclic voltammetry.

The potential of BTMDs to serve as a foundation for an e-tongue was assessed by polymerizing them onto glassy carbon rod electrodes, establishing 15 distinct working electrodes. Within this system, bare glassy carbon and Ag/AgCl functioned as counter and reference electrodes, respectively. Using the differential pulse voltammetry (DPV) method, we gauged the currents from various concentrations of homovanillic acid (HVA) in 0.1 M phosphate-buffered saline (PBS). Certain electrodes were sensitive enough to detect even low HVA concentrations. Techniques, such as PCA and clustering, were employed to pinpoint the most effective sensor array combinations.

SC15

Electrochemical Aptamer-Based Sensors for the Label-Free Detection of Pathogen Bacteria

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Detecting infectious pathogens, such as *Campylobacter jejuni* and *Staphylococcus aureus*, is a priority in the biomedical field to give an early and accurate diagnosis.[1] We aimed to develop two electrochemical sensors based on aptamers (APTs), single-stranded DNA oligonucleotide sequences that can specifically bind with high affinity to their target: the ONS-23 APT for *C. jejuni* cells and the PA#2/8 [S1-58] APT for *S. aureus* protein A (PrA).[2,3]

Carbon-based screen-printed electrodes (SPEs) decorated with Au nanoparticles via chronoamperometry and commercial Au SPEs were employed for the functionalization with the thiolated APTs. The SH-functionalized APTs without any label were immobilized onto the surface by multi-pulsed amperometry, followed by the blocking of unbound sites with 6-mercaptohexanol to avoid non-specific interactions using the same technique. Optimization was conducted to determine the optimal experimental conditions, including electrode surface, electrolyte composition, and electrochemical technique. The modifications after each step were monitored by differential pulse voltammetry and electrochemical impedance spectroscopy with the help of a ferro/ferricyanide redox probe. Scanning electron microscopy was also performed to confirm the changes in the morphology and capture of targeted bacteria. Affinity studies of the PA#2/8 APT to PrA were carried out by surface plasmon resonance.

To assess the performance of the aptasensors, multiple dilutions of *C. jejuni* NCTC 11322 and *S. aureus* ATCC 25923 strains cultivated in selective media were tested. The quantitative determination was performed by measuring the difference in the signal of the redox probe before and after incubation with the bacteria samples and correlating with the microbiological count method. The resistance to charge transfer in the impedance studies increased proportionally with the tested concentrations while the intensity of the current in voltammetry decreased. The performance of the aptasensors was also assessed with good recoveries in real samples: wastewater and human serum.

Both developed aptasensors showed promising results for detecting *C. jejuni* cells and protein A (as a target of *S. aureus*) in environmental and biological samples.

Acknowledgments:
The research was supported by the H2020 PathoCERT project, grant no. 883484, by the CNCS-UEFISCDI, project no. TE 89/23.05.2022 and by the UMF Iuliu Hațieganu internal grant no. 773/4/11.01.2023.

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K24

Analysis of Heterogeneous Hydrogen Evolution with Scanning Electrochemical Microscopy

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The importance of efficient hydrogen production utilizing an excess of hard-to-store electricity is well understood. Enormous effort has been put into better understanding and facilitating the anodic part of electrochemical water splitting since the oxygen evolution reaction kinetics substantially limits the overall performance of the electrolyzers.[1] However, the kinetics of hydrogen evolution reaction (HER) is also far from thermodynamic reversibility and requires the application of overpotential, especially when a platinum catalyst is absent.[2] There is still room for improvement in water electrolysis on the cathode site. On the other hand, HER can be undesirable when one wants to study or drive electrode processes at low potentials, e.g., electroanalysis or electrodeposition of nonnoble metals or carbon dioxide reduction.[3] The latter process yielding valuable products can be efficiently driven homogeneously with hydrogen.[4,5] Therefore, microscale analysis of HER electrocatalysts and materials for low potential electrodes, high-resolution localization of HER active sites, and evaluation of kinetic parameters of HER are highly desirable. We will show and discuss the results of kinetic analysis and imaging of HER electrocatalysts with feedback mode SECM. Electrons for HER in the studied samples are delivered by bipotentiostatic polarization, i.e., no electron donor for HER is generated at the SECM tip as in previous works with feedback mode.[6,7] HER is triggered on the polarized sample by a localized pH drop induced by hydrogen oxidation at the tip.

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K25

Surface Modification via Scanning Electrochemical Probe Microscopy (SEPM): from Molecular Catalyst Arrays to Antimicrobial Surfaces

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Scanning (electrochemical) probe microscopy (SEPM) has a long tradition in surface modification, dating back to manipulating single atoms via scanning tunneling microscopy.[1] Nowadays, micro- to nanoscale modifications using *in situ* deposition or etching processes via scanning electrochemical microscopy (SECM) or single and dual-barrel nanopipette-based SEPM techniques like scanning electrochemical cell microscopy (SECCM) have gained significant attention, as localized, maskless, three-dimensional surface modifications can be achieved.[2,3] Moreover, S(E)PM techniques can be used to characterize the obtained surface structures with respect to physicochemical and electro(analytical) properties.

In this contribution, we explore SECCM for the (electro)deposition of silver nanoparticles (AgNPs) arrays. AgNPs have shown potential against both multidrug-resistant (MDR) bacteria and biofilms due to their broad-spectrum antimicrobial properties based on a synergistic effect of the NPs themselves and the released Ag(I) ions.[4,5] The effect of Ag(I) ion release on the early stage of biofilm formation and its effects on single bacteria adhesion and integrity will be highlighted. Moreover, S(E)PM techniques like SECM, SECCM, and atomic force microscopy (AFM) are attractive for screening experiments of, e.g., heterogenized molecular catalysts in light-driven water splitting.[6] Screening the hydrogen evolution reaction (HER) of earth-abundant catalysts (CAT) like cobaloxime salts and co-deposition of ruthenium-based photosensitizer (PS) and CAT for light-driven hydrogen evolution is presented by depositing nano- and microstructures and arrays with different compositions. *In-situ* screening of hydrogen (H_2) evolution activity via SECM will be demonstrated. The activity in dependence of the composition and possible degradation studied via AFM will be discussed.

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K26

Unraveling the Mechanism of Aryldiazonium Reduction: Evidence and Quantitative Analysis of Reactive Intermediates and Byproducts

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Aryldiazonium electroreduction, introduced two decades ago, has become one of the most popular methods for functionalizing a broad range of substrates.[1] Despite being a simple and efficient method, the reduction mechanism has remained unclear. It is due to the involvement of highly reactive intermediate species (RIS) that are not well understood or controlled. In this study, we combined electroanalytical techniques such as ultrafast cyclic voltammetry, real-time spectroelectrochemical monitoring, and scanning electrochemical microscopy (SECM) with modeling approaches to investigate the 4-nitrobenzene diazonium reduction mechanism in depth. On the one hand, ultrafast cyclic voltammetry suggested the existence of the aryldiazenyl radical through a stepwise reduction of the aryldiazonium, and this was further confirmed by resolving the structure of a transient radical trapped via X-ray diffraction.[2] On the other hand, spectroelectrochemical experiments employing the mediated reduction of aryldiazonium through homogeneous redox catalysis (associated with EC' mechanisms) indicated the presence of relatively stable intermediates that were not completely understood. To further unravel this mediated reduction mechanism, the SECM in the feedback mode[3] combined with numerical simulations was employed. It revealed the existence of an irreversible reaction between the aryl radical and the redox mediator as a significant side reaction.[4]

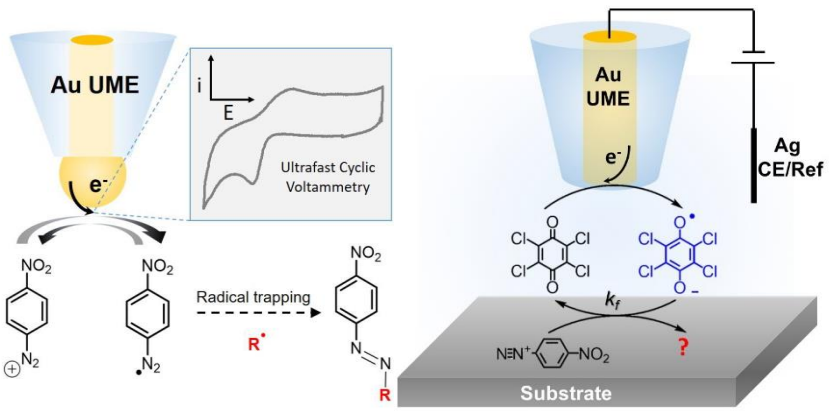

Figure 1. Investigation of the 4-nitrobenzene diazonium reduction mechanism.

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K27

Electrochemical Sensing of Clinically Relevant Proteins by Molecularly Imprinted Polymer-Modified Electrodes

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Nowadays, in healthcare, accurate and timely analysis of complex environments is critical for making informed decisions and ensuring public health and safety. Many current analytical methods, including molecular diagnostics and chromatographic techniques, are time-consuming and require a centralized laboratory facility, expensive instruments, and skilled personnel. The COVID-19 pandemic has further emphasized the crucial role of rapid diagnostic tests in improving healthcare outcomes and accessibility, especially in responding to global health emergencies. Hence, significant progress has been made in developing biosensors and point-of-care testing (PoCT) devices over the past few decades. Nearly all currently used PoCT devices and biosensors adopt a biological recognition element, such as an enzyme, antibody, or DNA, that is interfaced with the transducer to provide the specificity for a targeted analyte. However, one of the major limitations of these recognition elements is their instability in various thermal and pH conditions, leading to limited applicability and shelf-life. In addition, their production is costly and often involves animals, a matter of concern.

The use of molecularly imprinted polymers (MIPs) as robust biomimetic receptors in sensing devices is an attractive approach to overcome limitations associated with biological recognition elements. Through molecular imprinting, MIPs are precisely engineered to bind target molecules by creating molecular cavities within a polymeric network. These cavities accurately mimic the size, conformation, and chemical functionalities of the respective molecules, resulting in a highly specific and efficient binding capability for the desired targets.

Here, I present electrochemical sensors developed by my research group, which have been endowed with selectivity through modification by the MIP films providing rapid detection of (1) brain-derived neurotrophic factor (BDNF) as a potential neurodegenerative disorder biomarker,[1] (2) SARS-CoV-2 virus proteins NP and S1 as COVID-19 diagnostic markers [2,3] and (3) envelop protein E2 of Hepatitis C virus as potential biomarker for Hepatitis C diagnostics and treatment.[4] The analytical performance of the sensors was evaluated using DPV in the presence of a redox probe solution. The results demonstrated the sensor capability to detect the respective target protein in both buffer solutions and real biological samples with acceptable sensitivity at relevant concentration ranges. In essence, the electrochemical characteristics of the sensor can be easily handled by a portable potentiostat, allowing on-site measurements, thus holding a great potential as a PoCT platform for rapid clinical diagnostics.

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SC16

Electroanalytical Screening of Clozapine (Date and Rape Drug) in Soft and Hard Drinks at Electrified Liquid-Liquid Interfaces

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Benzodiazepines (BDZ) are psychoactive chemicals renowned for their ability to induce sedation and aid sleep; thus, they are prescribed to treat a range of clinical conditions (e.g., anxiety, insomnia, alcohol withdrawal).[1] Some BDZ and their structural analogues are reported to be used as illicit drugs and are subjected to strict regulations.[2] A combination of BDZ and alcohol was mostly related to drug-facilitated crimes such as robbery and sexual assaults.[3] Given these concerns on the social, health, and economic complexity of BDZ drugs, it is necessary to develop easy yet reliable assay tools to screen BDZ in food products, especially soft and hard drinks. To this, we aimed to develop an electrified liquid-liquid interface (eLLI) based rapid screening tool to assay BDZ drugs in soft and hard drinks.

We have studied the physiochemical, electroanalytical, and interfacial properties of clozapine (CZ – a BDZ drug) at eLLI. Studied experimental variables include ethanol concentration, pH of the aqueous phase, CZ concentration, electrochemical parameters, and direct influence of soft and hard drinks composition on the resulting electroanalytical output of the eLLI. CZ was interfacially active after the protonation of an amine group, which is a part of the drug molecular formula. The resulting ion transfer across the interface was studied with cyclic voltammetry. Parameters such as the standard Galvani potential of ion transfer reactions, CZ diffusion coefficient, partition, and distribution constants were calculated and tabulated. Next, the effect of ethanol addition to the aqueous phase on the interfacial stability and interfacial activity of CZ was studied in detail to obtain key analytical parameters such as sensitivity, LOD, and LOQ of the system. Further, the effect of pH on the partition of CZ ions between the interfaces is studied, and the findings are in line with that of theoretical calculations. The interfacial activity of CZ at eLLI formulated with soft and hard drinks (apple juice, vodka, vodka with an apple juice, wine, and beer – used as the aqueous phase) is studied in detail to provide essential analytical parameters including sensitivity, LOD, LOQ, and the selectivity pertaining to each system. These findings unveiled that each eLLI made of different soft and hard drinks has its own electrochemical profile and working parameters, hence the interfacial activity. Nevertheless, we have defined the optimal parameters for drug determination in the soft and hard drinks. The eLLIs-based system has shown adequate reliability in the rapid determination of CZ in spiked drinks samples. We also present our preliminary data on 3D-printed eLLI micro-supports used to miniaturize the entire determination platform. To close, this study has demonstrated the ability of eLLI in the successful determination of CZ in various soft and hard drinks and opened up new avenues for rapid on-site screening of these hard and soft drinks for CZ spiking.

Acknowledgments:
ST Balamurugan Thangaraj acknowledges Horizon EUROPE; HORIZON-WIDERA-2022-TALENTS-02-01 – Fostering balanced brain circulation – ERA Fellowships, GRANT AGREEMENT Project 101090335 – e-gainstRapeDrugs for funding.

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K28

Mechanical and Thermal Engineering of Functional Nanomembranes

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Continuous miniaturization of electronics, increasing computing power and data transmission speed, an alternative to silicon-based electronics, and obtaining new sources of clean energy are among the most vital challenges in physics, chemistry, and material engineering. The search for new materials, structures, and composites that can meet these requirements has contributed to the spectacular development of nanoscience and nanotechnology in the last two decades. What is essential, the search for new nanomaterials with application potential is often a compromise between excellent properties and incurred energy and environmental costs.

In this talk, I will present the results of experimental research focused on such topics as (i) polydopamine membranes for ultra-fast light-to-motion conversion,[1] (ii) silicon thermal diode,[2] (iii) elastic size effect in $MoSe_2$,[3] (iv) GHz signal filtering in 2D Phononic Crystals[4] and (v) mechanical reinforcement of colloidal crystals by a cold soldering process based on polymer plasticization using supercritical fluids.[5,6]

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K29

Simple Systems for Electrochemical Ion Sensing

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Over a decade ago, paper-based devices revolutionized the idea of Lab-on-a-chip systems, freeing them from the use of pumps, allowing easy and on-chip sample pretreatment, sample mixing, and storing of reagents.[1,2] The idea of simple systems goes beyond the use of paper towards the design of measurement setups that are easier to use and prepare, cheaper, and more versatile regardless of the material used.

Here, we would like to present two such systems for ion-sensing. First, presented in Fig. 1A, it allows for faster and more stable measurements of ion transfer at the classical polarizable interface, using reduced amounts of reagents. Using a spectrophotometric cuvette and capillaries pulled from Pasteur pipettes, we were able to prepare a 4-electrode cell, which uses a few hundred microliters instead of 5–10 mL of each of the phases. A smaller interface stabilizes the signal faster, and reduced volume can be explored to analyze new recognition molecules. In this case, we have tested several organoboron compounds as ionophores, enabling the detection of fluorine.

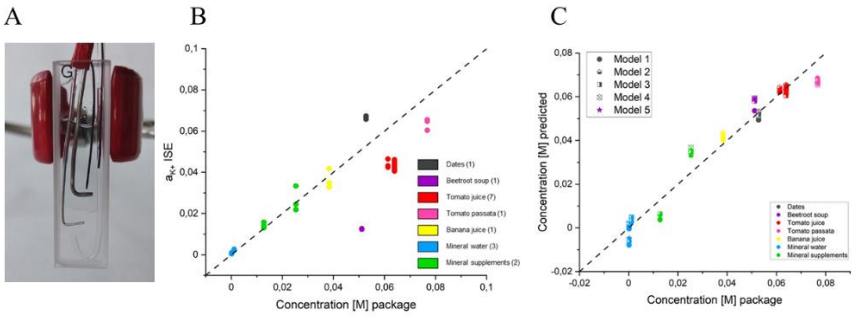

Figure 1. A. Simple cell for 4-electrode experiments at the interface of two immiscible solutions, B. real vs. the measured amount of potassium quantified using a single low-cost sensor, C. using a low-cost electronic tongue setup.

Setups for voltammetric sensing of ions, just as the one presented above, are still not popular in the scientific community, and ion sensing is primarily accomplished through potentiometry. We have prepared low-cost ion-selective potentiometric electrodes using syringes and applied them to measure potassium in different food products, including pharmaceutical supplements, mineral water from a few brands, tomato juices from different brands, banana juice, dried fruits, tomato sauce, and beetroot soup concentrate. Measurements agreed with the concentration calculated from the information given on the package for mineral water samples, pharmaceutical supplements, and banana juice. For other products, the deviation reached up to 75% of the expected value (Fig.1B). To remediate this problem, we have constructed an electronic tongue-sensor array coupled with a machine-learning algorithm based on the original low-cost potassium electrode and additional sensors that could account for the different ionic compositions of the food products (Fig.1C).

Acknowledgments:
Authors would like to thank National Science Centre Poland (NCN) Sonata 2020/39/D/ST4/02256 project.

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K30

Drugs, Membranes, 3D Printing and Sensing at Electrified Soft Junctions

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The title of this lecture combines four topics that we (E@SI team) have been focused on for the last three years: (i) electroanalytical detection of illicit drugs, (ii) synthesis and application of porous membranes/pores as a sensing unit component, (iii) 3D printing assisting sensing units fabrication, and (iv) electrified liquid-liquid interface being the transducing element of most of the developed sensing protocols.

In most cases, the detection at the electrified liquid-liquid interface is governed by the partitioning of the target ionic species from one phase to another upon applying the Galvani potential difference. The value of the Galvani potential difference at which the ions undergo potential-controlled ion transfer is directly related to the analyte hydrophilicity/hydrophobicity. This property governs the detection sensitivity. We have found that the illicit drugs themselves and interfering substances/cutting agents transfer at different values of the applied Galvani potential difference or (interfering substances) do not give a signal at all.[1–3] We meticulously collect and compare obtained data to defined optimized detection protocols.

Also, a lot of our attention is given to the optimization of the sensing unities by adjusting their geometry, size, and dimensionality. We have adopted 3D printing to create electrochemical cells[4,5] and electrochemical arrangements, allowing for the electrified liquid-liquid interface miniaturization[6] and downscaling sample consumption.[7]

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SC17

Transfer of Sulfate Ions Between Immiscible Liquids at the Three-Phase Junction Using a Novel Compound

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Ion transfer between two immiscible electrolyte solutions (ITIES) is an excellent tool for detecting a large number of different analytes,[1] including molecules that are not redox active. Unfortunately, sulfate ions are highly hydrophilic, which makes their detection in an ITIES system practically impossible.

We show that we can detect the transfer of sulfate ions at a three-phase junction using oxidation reactions of a novel compound (Figure 1) in the organic phase. We performed measurements of the transfer of ions in regular electrochemical cells, with a small organic drop deposited onto the surface of a glassy carbon electrode. This kind of setup is a great tool for investigating both facilitated and non-facilitated cation transfer processes.[2]

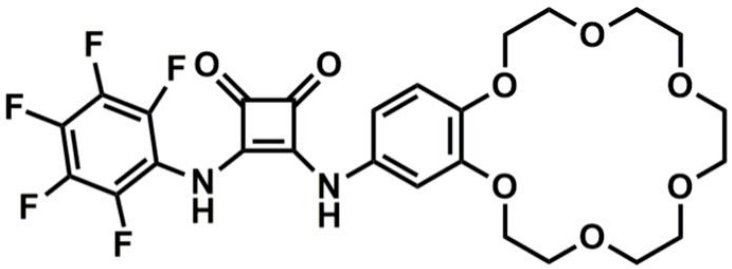

Figure 1. Structure of an ionophore.[3]

We evaluate the compound for the transfer of sulfate ions and its selectivity towards other anions. These measurements demonstrate the potential of applying ion-transfer voltammetry in the characterization of novel organic compounds and sensing.

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Tuesday, November 7

08:00–09:00		**Breakfast**
09:00–10:40		**Morning session 1** Chairs: E. Witkowska-Nery / P. Niedziałkowski
09:00–09:45	T06	**Sławomir Sęk** Exploring Surface Films of Peptides and Oligourea Foldamers for Material Applications and Molecular Switching
09:45–10:05	K31	**Piotr Pięta** Size-Dependent Effects of Amyloid Beta (Aβ) on a Model Brain-like Membrane
10:05–10:25	K32	**Lars Jeuken** Hybrid Polymer-Lipid Membrane Modified Electrodes
10:25–10:40	SC18	**Mostafa Torabi** Electrochemistry of Proteoliposome Derived Lipid Bilayers: HMG CoA Reductase and its Inhibition by Statins
10:40–11:10		**Coffee break**
11:10–11:45		**Morning session 2** Chairs: S. Arnaboldi / S. Sęk
11:10–11:30	K33	**Yolina Hubenova** Metabolic Pathways' Components Participating in the Cellular Response of a Biofilm to the Electrode Polarization
11:30–11:45	SC19	**Rafał Zbonikowski** Interfacial Colloidal Stimuli-Responsive Composed of Nanoparticles Decorated with Poly(N-Isopropyl Acrylamide) (PNIPAM)
11:45–12:00		**Closing ceremony**
12:00–13:00		**Lunch**
13:30		**Departures**

T06

Exploring Surface Films of Peptides and Oligourea Foldamers for Material Applications and Molecular Switching

Sławomir Sęk,[a] Karolina Pułka-Ziach,[b] Anna K. Puszko,[b] Joanna Juhaniewicz-Dębińska,[a] Paulina Bachurska,[b] Damian Dziubak,[a] Arkadiusz Grempka[a]

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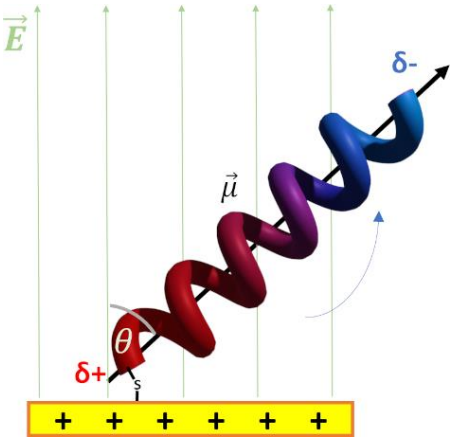
Peptides possess characteristics that allow them to be excellent functional polymers. Their simple synthesis, easy activation and condensation, metal and cofactor recognition, and the ability to self-assemble position peptides make them potential candidates for fundamental prebiotic roles. Evidence suggests that peptides could have played a crucial role even before being encoded by polynucleotide matrices. Their potential functions encompass catalysts and structural nodes in the early stages of life's evolution, emphasizing the potential contribution of peptides to the emergence of functional polymers. Currently, we can obtain peptides through synthetic means, and a growing understanding of the relationship between the structure of proteins and their function enables the design of specific peptide sequences that possess defined motifs and functions. Furthermore, the structure and function of peptides can be mimicked, to some extent, by applying so-called foldamers that possess a specific and defined three-dimensional structure or conformation due to the presence of non-covalent interactions within the molecule itself. Foldamers have gained significant attention in the fields of materials science, chemistry, and biology due to their ability to mimic the folding behavior of biomolecules like proteins and nucleic acids.[1] They can be designed to exhibit specific functions, such as molecular recognition, catalysis, or acting as molecular switches. Helicomimetic oligourea foldamers represent a versatile class of compounds with wide-ranging potential applications. However, their utilization in materials science remains largely unexplored. The chemical accessibility of urea-based monomers enables the synthesis of oligoureas with side chains analogous to natural amino acids, providing remarkable robustness and tunability. Unlike polypeptides, the folding process of oligoureas is independent of the side chain nature, making them highly adaptable. Even four residues are sufficient for complete stable helical turn formation in oligoureas. These exceptional attributes render oligoureas highly appealing for the design of functional materials. This lecture will undertake a comprehensive comparison between the characteristics of surface-confined films formed on gold substrates by peptides and oligoureas. The focus will be on aspects such as thickness-dependent conductance, mechanisms governing electron transport, and the ability to rectify current.[2] Additionally, the influence of an electric field on the motion of adsorbed molecules on the electrode surface will be discussed, as well as its interplay with the charge distribution along the molecule.[3] These insights provide a pathway toward the prospective deployment of peptide/foldamer films as materials endowed with properties that respond to external stimuli, further enhancing their potential for applications in molecular actuation and switching systems.



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K31

Size-Dependent Effects of Amyloid Beta (Aβ) on a Model Brain-like Membrane

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Alzheimer's disease (AD) is one of the most common types of dementia associated with abnormalities of misfolding and overproduction of amyloid β (Aβ) peptides. These abnormalities lead to the aggregation of A and the formation of pathogens responsible for developing this disease. The fundamental structural and mechanistic details by which misfolded A causes neurodegeneration in AD have not been fully delineated.

Amyloid β (Aβ) is a small protein that aggregates in a nucleation-polymerization manner. During the aggregation, it forms different molecular weight forms, ranging from monomers, oligomers, and protofibrils up to mature fibrils, and each of these forms has a unique behavior. At first, mature fibrils of Aβ were thought to be correlated with AD, but recent studies suggest that Aβ oligomers exhibit the highest toxicity towards cells. Several mechanisms of Aβ toxicity were proposed, like pore formation, detergent-like solubilization, and membrane thinning mechanism or combination of these. On the other hand, some studies suggest that cell membranes can act as a template for Aβ aggregation and accelerate the process. So, the Aβ-cell membrane interaction requires more studying to be wholly understood.

We used AFM, EIS, and PM IRRAS to study the interaction mechanism of 42-amino acid-long Aβ with a model cell membrane. For this purpose, we deposited a phospholipid bilayer, which resembles the composition of human brain cell walls, onto solid substrates (mica or Au(111)). All studies were performed in a buffer solution of pH = 7.4. We utilized a methodology that allows us to elucidate the phenomenon occurring both on the membrane surface and inside the membrane under the influence of the toxic effects of Aβ of different sizes. The results showed that Aβ interacts with the membrane differently depending on the Aβ molecular weight form.

K32

Hybrid Polymer-Lipid Membrane Modified Electrodes

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Bacterial respiratory membrane enzymes are a novel target space for new antibiotics, but drug development would benefit from stable enzyme assays in native-like membrane environments. We have shown that bioelectrochemical platforms in which a lipid membrane is supported or tethered to an electrode surface can be used to monitor the activity of respiratory, quinone-converting enzymes within their native membrane and the effect of inhibitors. In these systems, electron transfer between the electrode and membrane enzymes is mediated by the native quinone pool (e.g., ubiquinone or menaquinone). I will briefly present examples of our studies of type-2 NADH dehydrogenase and cytochrome bd. For these bioelectrochemical platforms to be used for drug screening, further enhancements in long-term stability would be beneficial. Reconstituting membrane enzymes in hybrid membranes, which are mixtures of natural lipids and synthetic amphiphilic polymers such as diblock copolymer poly(butadiene-*b*-ethylene oxide) (PBd_{22}-*b*-PEO_{14}), have been shown to strongly enhance the stability of membrane enzymes. I will present our characterization of electrodes that are modified with hybrid membranes using impedance spectroscopy, atomic force microscopy, and quartz-crystal microbalance with dissipation (QCM-D). Although planar membranes were successfully formed, the electrochemical oxidation and reduction of lipophilic quinones were significantly impaired compared to lipid-only membranes. Novel membrane-modified systems will be discussed to elevate this bottleneck in drug screening.

SC18

Electrochemistry of Proteoliposome Derived Lipid Bilayers: HMG CoA Reductase and its Inhibition by Statins

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Electrochemical methods are used to characterize transport phenomena in the presence of membrane proteins, monitoring changes in their catalytic properties and their activity in the presence of activators and inhibitors. Since membrane proteins are fully active in their pristine environment – lipid membrane, the electrochemical investigation of enzymes should be carried out when they are present in an appropriate lipid membrane and deposited on the electrode surface.[1]

Here, HMG-CoA reductase (HMGR), the membrane protein responsible for cholesterol synthesis and its related coenzyme (HMG-CoA) were incorporated into a lipid bilayer obtained by spreading proteoliposomes on the gold electrode surface modified with a thioglucose.[2] $NADP^+$ is formed in the enzymatic reaction when HMG-CoA is reduced to its immediate product, mevalonate, which is further transformed into cholesterol. The reconstitution of HMG-CoA reductase and its proper work was investigated by following the $NADP^+$ reduction peak with the assistance of the ABTS using cyclic voltammetry and electrochemical impedance spectroscopy. The activity of the HMGR was studied over time and in the presence of fluvastatin as the example of the HMGR reductase inhibitor commonly used in the treatment of hypercholesterolemia.

The prepared modified gold electrode with proteoliposome is illustrated schematically in Figure 1. While the CV obtained on the modified electrode in PBS 7.4 solution was almost featureless (displayed just a charging-current background) and the Nyquist plot has a high R_{ct}, the obtained CV in PBS solution including 3 mM NADPH shows a reduction in faradaic current and decreased R_{ct} that can be attributed to the electrochemical reduction of the $NADP^+$ formed in the catalytic process. After injection of fluvastatin into the measuring solution and exposure of HMG CoA reductase to the inhibitor drug, the enzyme active site is blocked by the drug. Therefore, the amount of produced $NADP^+$ decreases, so does its reduction peak. Also, an increase in R_{ct} is observed in the Nyquist plot.

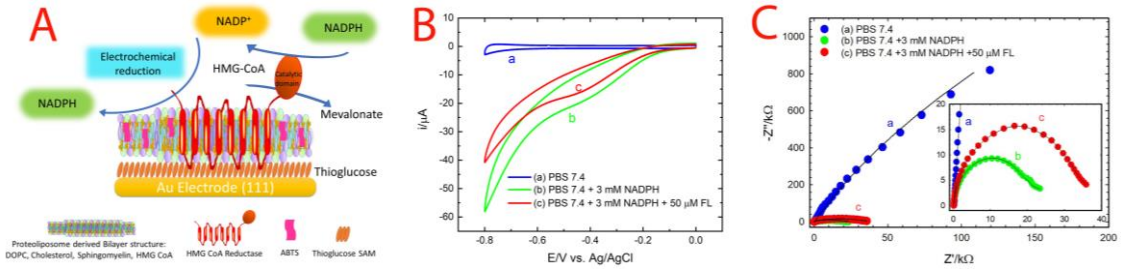

Figure 1. Schematic illustration of the proteoliposome-derived electrode modification and monitoring of the catalytic process by CV and EIS in the absence and presence of statin.

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K33

Metabolic Pathways' Components Participating in the Cellular Response of a Biofilm to the Electrode Polarization

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The exoelectrogenic properties of gram-negative bacteria are well established, while those of gram-positive bacteria still need detailed investigation.

This keynote lecture summarizes the electrochemical data collected on bacteria belonging to the genera *Paenibacillus*.[1–3] Two species were isolated from the anode surface of a long-term operated sediment microbial fuel cell (SMFC), identified,[4] and tested as separate cultures of the respective biocatalyst. The electrode surface was modified by forcing the bacteria to adhere and form a biofilm. The electrochemical activity of mature bacterial biofilms was investigated using cyclic voltammetry, differential pulse voltammetry, and electrochemical impedance spectroscopy. Different poising potentials lead to markedly diverse redox behavior, suggesting that different components of the branched anaerobic metabolic pathways are involved in regulating the cellular response and extracellular electron transfer. Indeed, the gene expression analyses performed using seven specific primers for respiratory gene products show that by applying a specific potential to the biofilm-covered electrode, we are able to up- or down-regulate the cell metabolism. By matching the electrical parameters with the genetic parameters, the bioelectrochemical system becomes a biosensor for the degree of fermentation and respiratory processes occurring within the bacteria.

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SC19

Interfacial Colloidal Stimuli-Responsive Composed of Nanoparticles Decorated with Poly(*N*-Isopropyl Acrylamide) (PNIPAM)

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Recently, nanotechnology has moved from equilibrium self-assembly toward dynamic self-assembly and stimuli-responsive systems. Materials active in the presence of an external stimulus or requiring a constant energy supply are going to be the future of new complex nanotechnological systems.[1] Our research focuses on the formulation of interfacial (pseudo-2D) colloidal stimuli-responsive systems with potential application to fabricate adjustable membranes or active and reconfigurable coatings.[2]

Synthesised Fe_xO_y@SiO_2 nanoparticles capped with thermo-responsive PNIPAM (Figure 1) were used as a building block with almost binary properties due to the two temperature regimes. We established the procedure of successful deposition of hydrophilic nanoparticles at the air/water interface (Langmuir film) and examined the behaviour of the system upon temperature change, compression, and the ionic force of the subphase. The surface pressure and surface potential measurements were supported by SEM, BAM, DLS, profilometry, and theoretical calculations.

We discussed the design of the nanoparticles in the context of possible interfacial phenomena. The different, controlled aggregation was observed due to certain stimuli, especially the temperature regime. The nanoparticles performed reversible self-assembly between a uniform (high temperature) and a non-uniform (low temperature) state. Short oligomer chains (ca. 5 nm) were able to control nanoparticles (65 nm or 90 nm) by "closing" and "opening" above and below the critical temperature (around 32°C). As expected, the area occupied by a single nanoparticle on the ultra-pure water surface was decreased above 32°C. However, the system changes its behaviour significantly by increasing the concentration of KCl dissolved in the subphase. We discuss the interactions within the system to allow further development of stimuli-responsive system designs.

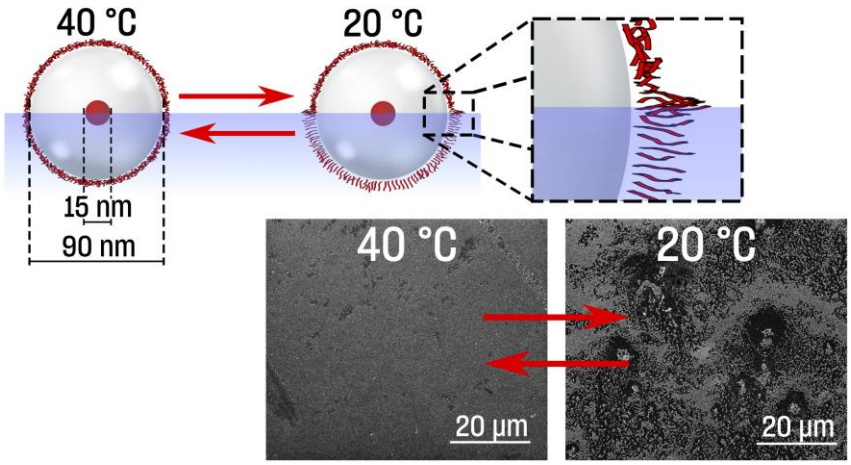

Figure 1. Stimuli-responsive Fe_xO_y NPs capped with PNIPAM. SEM images of monolayers of the nanoparticles at different temperatures. Adapted with permission (CC-BY 4.0). Copyright 2023, American Chemical Society.

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Poster session

Saturday, November 4
17:00–19:00

P01

Addressing Non-Specific Adsorption in Aptasensors for Protein Aggregation Studies

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Lysozyme is an antibacterial protein present in many body fluids and a model for studying protein aggregation concerning degenerative diseases. Increased lysozyme levels in body fluids are nonspecific indicators of inflammation and infection,[1] while amyloid aggregates of lysozyme deposited on kidneys are a hallmark of a rare genetic disease called familial amyloidosis. The detection of proteins with biosensors is faced with the complex problem of non-specific adsorption (NSA), leading to reduced sensitivity.[2] The issue is exacerbated in aggregated protein samples. Aiming to develop electrochemical aptasensors for detecting both monomeric and aggregated lysozyme, we report an initial study into the prevention of NSA.

Following a typical aptasensing design, we immobilized a specific lysozyme DNA aptamer on a gold electrode by chemisorption, making a self-assembled monolayer (SAM), and used backfilling with thiolated molecules such as mercaptohexanol (MCH), mercaptoundecanol, and polyethylene glycol (PEG) derived thiols, along with bovine serum albumin (BSA). Measurements were conducted by cyclic voltammetry (CV) using the ferrocyanide/ferricyanide (HEX II/III) couple. Adsorption for 1 h at room temperature was conducted in parallel with electrochemical deposition of thiolated molecules by pulsed amperometry.[3] Lysozyme amyloid fibrils were obtained by incubation at 60°C in acidic conditions for 3 days and were characterised by atomic force microscopy (AFM), spectrophotometry using Congo Red, and fluorimetry with thioflavin T dye.

Aptamer-functionalised electrodes were compared with control ones, coated exclusively with mercaptohexanol. The successful functionalisation with thiol-ended aptamers by the electrochemical deposition procedure was confirmed by Raman spectroscopy analysis. Cyclic voltammetry measurements emphasized very similar changes for the peak currents of HEX II/III recorded with aptamer-functionalised and control electrodes upon incubation with several concentrations of lysozyme, thus indicating significant NSA. A more detailed study with various thiol-coated Au SPEs led to the observation that mercaptoundecanol was the most efficient among the tested compounds for both the monomeric and fibrillar forms of lysozyme. Lower efficiency was obtained for coatings of a short thiol with four ethylene glycol groups and for BSA.

In perspective, in order to achieve the electrochemical detection of lysozyme in monomer and fibril state with high sensitivity, the electrochemical deposition of mixed coatings of MCU, PEG4SH, and BSA will be investigated.

Acknowledgments:
Financial support by the Romanian Executive Agency for Higher Education, Research, Development and Innovation (UEFISCDI), PN-III-P4-ID-PCE-2020-2297 E-MAP project, contract 84/0.9.02.2021 (for A.V and RMB) is gratefully acknowledged.

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P02

Mixed Aptamer and Thioaromatic Coating as Antifouling and Specific Interface for Electrochemical Assisted Monitoring of Food Allergen

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Food allergies have become a global issue, affecting over 220 million people worldwide.[1] Ara h1 is one of the major allergens found in peanuts and can trigger an immunological response in more than 50% of the allergic population, representing the first leading cause of anaphylactic fatalities worldwide.[2] Taking into consideration the ongoing demand for analytical strategies for on-site sensitive detection of food allergens, this work presents a strategy for the sensitive and rapid detection of the presence of Ara h1 protein in food products by enabling an electrochemical approach based on single-stranded DNA aptamer (Apt).

The design of the electrochemical aptasensor for Ara h1 envisioned immobilization of the aptamer by the insertion method. First, a layer of *p*-aminothiophenol (*p*-ATP) was deposited on the surface of screen-printed gold electrodes, further improving the Ara h1 specific Apt insertion in a controlled manner and reducing the fouling effects at the electrode surface. Stepwise modifications of the gold surface and optimum parameters for developing the mixed *p*-ATP and Apt assembly were monitored by cyclic voltammetry, differential pulse voltammetry (DPV), and electrochemical impedance spectroscopy (EIS). The resulting disposable aptasensor allowed for indirect electrochemical detection of Ara h1 in the presence of 5 mM ferro/ferricyanide as a redox probe. The quantification of Ara h1, based on the electrochemical response generated upon Apt-target interaction, was monitored by EIS and DPV in 1–150 nM concentration range, obtaining limits of detection in the nanomolar domain. Selectivity studies against proteins commonly found in food products were performed, and the aptasensor was successfully applied to real sample analysis.

Acknowledgments:
This work was supported by a grant from the Romanian Ministry of Education and Research, CNCS-UEFISCDI, project number PN-III- P1–1.1-PD-2019–0631, within PNCDI III.

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P03

The Charge Transfer Kinetics Enhancement of 3D Printed Electrodes: the Role of Polymer Matrix

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The 3D printed electrode surfaces must be activated by removing the outer layer of the polymer matrix and exposing the conductive carbon filler to improve the electron transfer efficiency at the electrode/electrolyte interface. Surface activation can be carried out by immersing the electrode in an aprotic solvent, where the best results are obtained for dimethylformamide. Different activation routes include electrolysis in aqueous electrolytes or enzymolysis in proteinase K.[1]

Our group focused on a new surface activation process based on laser ablation. Nd:YAG[2] laser and femtosecond laser[3] were used for this process. After optimizing process parameters, we have reported that the laser ablation process effectively removes the polymer matrix from the carbon black poly(lactic acid) (CB-PLA) composite electrode surface, significantly enhancing the kinetics of the redox process and available electrochemically active surface area (EASA). In addition, the activation protocol is time-efficient and does not require the use of toxic chemicals. Femtosecond laser (FSL) offers significant advantages, allowing precise ablation with zero or negligible thermal influence on the surrounding material. An FSL ablation may thus constitute a promising approach to micro- and nanostructurization of 3D printouts.

After many tests carried out on commercially available conductive composites, we started creating our own 3D printing filaments with the addition of nanodiamonds dedicated to electrochemical measurements.[4] In our new approach, we decide to make copolymer matrix material consisting of PLA and polypropylene (PP) as a plasticizer and check how surface treatment as laser ablation influences charge transfer kinetics enhancement.

Acknowledgments:
The authors acknowledge the financial support from the National Science Centre (Republic of Poland) SONATA BIS 2020/38/E/ST8/00409.

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P04

The Peroxidase-like Nanocomposites as Hydrogen Peroxide-Sensitive Elements in Cholesterol Oxidase-Based Biosensors for Cholesterol Assay

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Peroxidase (PO; E.C. 1.11.1.7) is the oxidoreductase that catalyzes the oxidation of organic substrates in the presence of hydrogen peroxide as an electron acceptor. PO is widely used in different fields of science and industry, especially in analytics for H_2O_2 determination.[1,2] Catalytically active nanomaterials, in particular, nanozymes, are promising candidates for applications in biosensors due to their excellent catalytic activity, stability, and cost-effective preparation. Artificial enzymes having PO activity, especially PO-like nanozymes (NZs) or "nanoperoxidases" (nanoPOs), are promising substitutes for natural PO, especially in biosensors.[3,4]

Cholesterol (cholest-5-en-3β-ol, CHOL) is a crucial lipid molecule that fulfills different biological functions.[5] It plays a crucial role in maintaining the rigidity of cellular membranes and fluidity.[6] CHOL is an important component of the human brain and is necessary for signal transmission.[7] The increased cholesterol level in the blood serves as an important biomarker of cardiovascular disease.[8] The aim of the current research was to develop cholesterol oxidase-based amperometric bionanosensors using novel nanocomposites as PO mimetics. To select the most electroactive chemosensor on hydrogen peroxide, a wide range of nanomaterials was synthesized and characterized using cyclic voltammetry (CV) and chronoamperometry. Pt NPs were deposited on the surface of a glassy carbon electrode (GCE) in order to improve the conductivity and sensitivity of the nanocomposites. The most HRP-like active bi-metallic CuFe nanoparticles (nCuFe) were placed on a previously nano-platinized electrode, followed by the conjugation of cholesterol oxidase (ChOx) in a cross-linking film formed by cysteamine and glutaraldehyde.

The constructed nanostructured bioelectrode ChOx/nCuFe/nPt/GCE was characterized by CV and chronoamperometry in the presence of cholesterol. The bionanosensor shows a high sensitivity (3960 A M^{-1} m^{-2}) for cholesterol, a wide linear range (2–50 μM), and good storage stability at a low working potential, that is −0.25 V vs. Ag/AgCl (3 M KCl). The constructed bionanosensor was tested on a real serum sample. A detailed comparative analysis of the bioanalytical characteristics of the developed cholesterol bionanosensor and the known analogs is presented.

Acknowledgments:
This research was supported by the IIE-Scholar Rescue Fund and the Institute of International Education.

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P05

Electrochemical Characterization of Alpha-Hemolysin in Sparsely Tethered Bilayer Lipid Membrane Embedded in Bicelles

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Transmembrane proteins still challenge the understanding of their function within the membrane. Therefore, biomimetic systems need to be developed to understand such macromolecules better. The developed systems should provide a suitable environment for the membrane and the protein. Moreover, the process of protein incorporation should be relatively easy in such a system.

A combination of sparsely tethered bilayer lipid membrane systems and bicelles used as a precursor of lipid membrane fulfills the criteria. Modifying the gold electrode with small hydrophilic molecules and the tethered molecules enables the creation of a water-rich submembrane region between the lipid bilayer and the gold electrode. Such extra space makes a proper environment for membrane and protein and protects the protein from denaturation, which might occur during electrode polarization.[1] Bicelles belong to the lipid system initially used for structural studies of transmembrane proteins. The properties of bicelles enable the incorporation of proteins rather readily. Recent studies also show the possibility of using such membrane precursors to create lipid membranes on the solid substrate.[2]

Here, we demonstrate that the properties of the membrane prepared this way are analogous to those where the membrane was prepared by vesicle spreading. Furthermore, we investigated the effect of the alpha-hemolysin toxin on the membrane. The presented results prove that this protein retains its functionality in the biomimetic membrane upon insertion.[3]

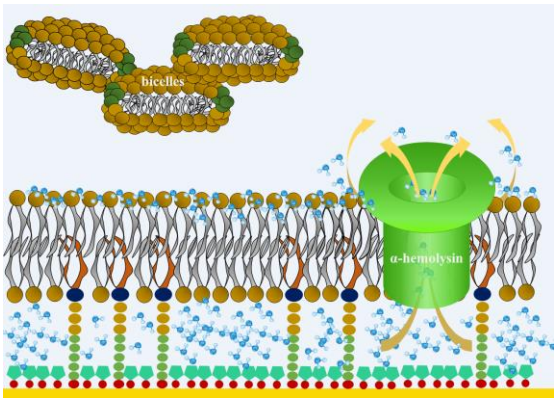

Figure 1. Influence of alpha-hemolysin on the model cell membrane formed by self-assembly of bicelles.

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P06

A Cold Active Aldehyde Dehydrogenase from Flavobacterium PL002 as a New Enzymatic Label for DNA Aptamers: a Preliminary Study

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Aptamer-based biosensing mechanisms often involve DNA probes labeled with catalysts (enzymes, nanozymes, DNAzymes) to obtain a high-output electrochemical or optical signal. Despite costs and stability limitations, natural enzymes remain the most powerful catalysts available.[1] In the context of a continuous search for new enzyme labels with interesting properties, we studied the potential of a cold-active aldehyde dehydrogenase from the Antarctic *Flavobacterium Pl002 (F-ALDH)* for the controlled labeling of a DNA aptamer for lysozyme.[2] The cold active recombinant enzyme functions in a wide temperature range, and the recombinant enzyme has a histidine tag attached to the *N*-terminal, with an affinity for the complex nickel-N_α,N_α-bis(carboxymethyl)-L-lysine hydrate complex (Ni-NAT).[3] The enzyme-tagged lysozyme aptamer was obtained by a four-step procedure involving (i) the preparation of a conjugate between the thiol-ended aptamer and N_α,N_α-bis(carboxymethyl)-L-lysine using maleimide; (ii) incubation with $NiCl_2$ to form Ni-nitrilotriacetic acid chelate; (iii) attaching the enzyme to the aptamer via nickel-histidine affinity; (iv) reaction product purification, i.e., the labeled aptamer by centrifugation through 30 kDa cut-off filter and size exclusion chromatography (SEC).

The absorbance values at 260 nm and 280 nm in the UV spectrum of the purified „labeled aptamer" indicated the successful attachment of F-ALDH to the aptamer, and the second confirmation was offered by the fluorescence of the reaction product, detected with the fluorescence detector during the SEC analysis. The binding to the aptamer resulted in a 23% reduction in the specific activity of F-ALDH compared to the free enzyme. In enzymatic activity measurements of lysozyme measuring the absorbance of *Micrococcus lysodeikticus* substrate at a plate reader, the labeled aptamer significantly inhibited lysozyme activity, indicating strong binding of the labeled aptamer. Attempts to measure the conjugate mass and obtain direct proof by gel electrophoresis were unsuccessful. Experiments conducted under optimal conditions to visualize the enzyme or the DNA enabled the identification of two components in the „labeled aptamer" solution, but no additional bands proved that aptamer was bound to the enzyme. While the preliminary data is encouraging, the labeled aptamer structure remains to be investigated by LC/MS. Appropriate storage conditions identified for preserving the catalytic activity of aptamer-bound F-ALDH and the binding affinity of labeled aptamer for lysozyme remain to be determined.

Acknowledgments:
The authors acknowledge the financial support from UEFISCDI, projects ERANET-M-ENZ4IFACES ctr. 166/2020 (for GN-P, CP, AV) and PN-III-P4-ID-PCE-2020-2297 E-MAP, contract 84/09.02.2021 (for AF).

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P07

Study of the Pumping Efficiency of Systems with Macroscopic Helical Chirality

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Chirality plays a crucial role in different research fields, ranging from medicine and materials science to physico-chemistry.

In this work, we have introduced artificial and macroscopically chiral soft pumps assembled by electrodepositing polypyrrole with a helical shape.[1]

The chiral systems were implemented as bipolar electrodes in bipolar electrochemical set-ups in order to study their pumping efficiency.

Compared to other systems activated by alternative external stimuli, pumping devices driven by an electric field are an interesting approach to controlling the flow rate and the direction of the injected liquid. However, electrically-driven soft pumps are still limited by the essential requirement of an electric contact necessary to activate their actuation.[2–4]

Herein, we have designed macroscopically chiral soft-helical systems activated in a wireless mode by means of bipolar electrochemistry.

In this set of measurements, the bipolar electrode was placed in different directions with respect to the electric field (parallel vs. perpendicular), considering the time that a drop of doxorubicin (dissolved in ionic liquid, IL) requires to pass from one side of the helix to the other.[1]

Combining the applied electric field with the electrical conductivity (an intrinsic feature of the polypyrrole) and their pumping ability makes these innovative bipolar soft pumps good candidates for multipurpose asymmetric detection with potentially high impact in analytical, biological, and pharmaceutical fields.

Acknowledgments:
This work has been funded by the H2020 European Research Council (ERC) under the HORIZON-ERC-2021 work program (grant agreement no 101040798, ERC Starting grant CHEIR).

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P08

Iron Hydroxide Hollow Spheres for Multienzymatic Reactions

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Enzymatic reactions are efficient, selective, and eco-friendly. However, some challenges in industrial applications, such as instability, still remain to be solved. Various protective carriers for enzymes have been developed, including polymeric hollow spheres (HSs). This poster presents the first example of inorganic HSs constructed under mild, biocompatible conditions, enabling the embedding of enzymes within the shells. A simple mixing of calcium carbonate ($CaCO_3$) particles and Fe^{3+} ions leads to the formation of iron hydroxide HSs (FeH-HSs). The encapsulated enzymes maintain their catalytic activity, and multienzyme cascade reactions are demonstrated, in which the open voids of FeH-HSs facilitate the efficient diffusion of reactants and reaction intermediates.

P09

On the Effect of the Insulin Aggregation Degree on its Interactions with Model Lipid Rafts

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Diabetes mellitus is a metabolic disease that currently affects more than 420 million people worldwide, and the World Health Organization predicts that the number of deaths caused by diabetes will double by 2030. Insulin forms insoluble fibrillary deposits at the site of repeated injections in diabetic patients.[1] Moreover, it is prone to aggregation in vitro, which makes it highly useful for studies of mechanisms of protein aggregation.

Here, we present the results of our studies on the interactions of insulin with model lipid membranes enriched in the ganglioside GM3. Gangliosides are naturally located in specific domains within the cell membranes called lipid rafts. These rafts, in turn, are presumed to be a binding site for amyloid-membrane interactions.[2] Specifically, GM3 has been implicated in the development of insulin resistance in T2DM.[3] Moreover, zinc is involved in the storage of insulin. Total zinc concentration in the pancreatic β-cells is one of the highest in the body, and the change in zinc concentration can also be associated with diabetes.[4] Therefore, the goal of this study was to verify how the presence of GM3 in the lipid biomimetic membrane and the presence of zinc ions affect the membrane behavior and membrane-insulin interactions.

Model lipid rafts were composed of 1,2-dioleoyl-*sn*-glycero-3-phosphocholine (DOPC), sphingomyelin (SM), and cholesterol (Chol) without GM3 and with the addition of 25 mol% GM3. The experiments were performed with insulin characterized by different aggregation degrees, from monomer to fibrils, which was confirmed by UV-Vis studies with thioflavin T. The interactions of insulin with model lipid membranes were studied on a monolayer model system by the Langmuir technique, and the substrate-immobilized bilayers were examined by the ATR-FTIR technique. The experiments performed using the Langmuir trough allowed us to determine the miscibility of the membrane components and the effect of insulin on membrane fluidity and stability, while ATR-FTIR measurements provided information on mechanisms of insulin-membrane interactions in time.

The results clearly show that monomeric insulin partially incorporates the external, hydrophilic part of the membrane, while the reorganization of the acyl chains was not observed. On the other hand, insulin aggregates are too bulky to incorporate into lipid membrane environments and interact mainly with the membrane surface. The effect of ganglioside GM3 was significant for interactions of insulin, both monomeric and aggregated, independently of the presence of zinc ions. The hexameric zinc-insulin complexes are not able to penetrate the lipid membrane. They accumulate on the lipid membrane surface and change the orientation of lipid molecules.

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P10

Determination of Bupropion Using Electrochemical Sensing Platform Based on Screen-Printed Carbon Electrode Modified with Plasma Polymerized Acrylonitrile Nanofilms

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The widespread use of electroanalytical techniques has led to a search for new electrode materials to develop electrochemical sensors. In order to provide the best characteristics of sensors, new functionalized electrode materials are designed, as well as novel methods of physical or chemical modification of substrate electrode surface are developed. The nanofilms obtained in the chemical vapor deposition process (CVD) are a particularly promising group of functional materials that could replace conventional materials used for electrode modification.[1]

The aim of the work was to develop an electrochemical sensing platform based on carbon screen-printed electrodes (SPCEs) modification with plasma polymerized acrylonitrile (pp-AN) nanofilms, for the determination of bupropion (BUP), an antidepressant drug whose intake has increased dramatically during the COVID-19 pandemic. For that purpose, plasma-enhanced chemical vapor deposition (PECVD) process was conducted in a parallel plate (13.56 MHz) plasma reactor for 2 min with discharge power of 10 W.[2] The surface topography and electrochemical properties of prepared sensors were investigated by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV). The electrochemical characteristics of pp-AN/SPCE was performed for the model redox pair $[Fe(CN)_6]^{4-/3-}$. Conducted research confirmed the excellent chemical stability, durability, wide potential window, and high signal-to-noise (*S*/*N*) ratio. The voltammetric response of pp-AN/SPCE for BUP was linear in two concentration ranges of 0.63–10.0 and 10.0–50.0 μmol L^{-1}, with a detection limit of 0.21 μmol L^{-1}. Satisfactory recoveries (96.2–102%) and good precision (RSD below 4.1%) obtained for environmental and biological samples confirmed the usefulness of the sensor for the analysis of various samples.[3]

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P11

Comparison of Different Methods of Electrode Modification Towards Human Chorionic Gonadotropin (hCG) Detection in Human Serum

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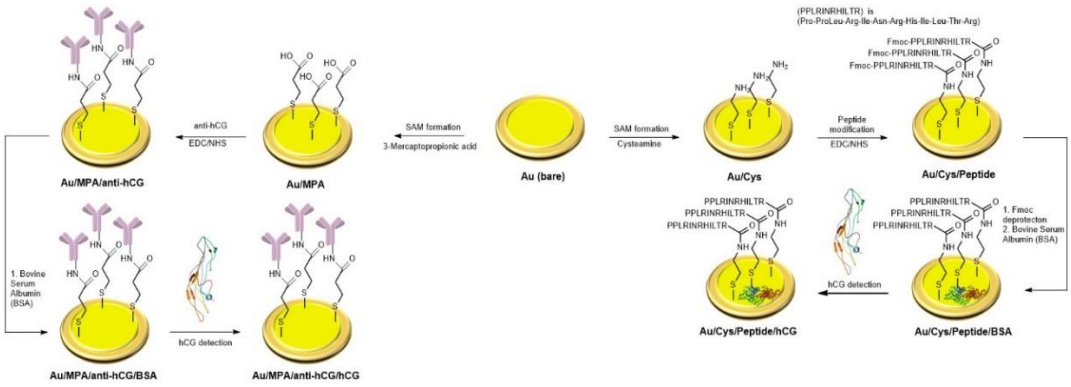
Human chorionic gonadotropin (hCG) is a hormone from the gonadotropin group produced during pregnancy by the embryo (specifically, the syncytiotrophoblast) and then by the placenta. Its main role is to maintain the function of the corpus luteum, a structure formed in the ovary at the site of the release of the egg, and then to maintain the production of progesterone.

Early hCG secretion is a marker of good embryonic development and indicates a good prognosis for the development of the pregnancy. It is, therefore, important to accurately measure hCG as early in pregnancy as possible when its levels are very low. The average serum level of hCG in a healthy pregnancy in the third week is about 0.26 ng mL^{-1}, and in the peak period of its secretion, it exceeds 10,000 ng mL^{-1}.[1] The hCG is also a factor involved in the pathomechanism of many pregnancy complications. The deficiency of hyperglycosylated hCG (the main form of hCG in early pregnancy) is considered to be the main factor of hypertensive pregnancy,[1] pre-eclampsia, or the development of pregnancy-induced hypertension (PIH), but also predicts poor hemochorial placentation growth or nutritional deficiency. The hCG level is also used in prenatal diagnostics for Down syndrome pregnancy risk estimation.[2]

In this work, we present a new approach to modifying a gold electrode, an oligopeptide (PPLRINRHILTR), and an antibody sensitive to the presence of the hCG hormone in a phosphate-buffered saline solution (PBS) and human blood serum.[3] Additionally, the above method was used for the reproducibility of the modified gold electrode to determine hCG.



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P12

Visualization of Molecularly Imprinted Cavities in Polymer Nanofilms by Gold Electrodeposition-Assisted Atomic Force Microscopy

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Molecularly imprinted polymers (MIPs) are at the forefront of synthetic receptor development for selective recognition of small and large molecular weight compounds. They can act as synthetic alternatives of biological origin affinity reagents, such as antibodies. Accordingly, they can be used for a wide range of applications based on molecular recognition, e.g., affinity assays, drug delivery, separations, and chemical sensing.[1] Besides holding the promise of low cost, thermal stability, and robustness, MIPs are especially appealing because they move the reagent development to the chemical lab, which offers unique advantages in terms of utmost control and reproducibility of the synthetic procedure. Advances in MIP synthesis, including surface imprinting, epitope imprinting, and mild synthetic conditions, allowed to target delicate proteins. However, many fundamental assumptions of protein MIP synthesis remained without explicit and direct confirmation, most notably the physical presence of the protein binding cavities. These are generally confirmed by the result of the binding event rather than by independent methods. One reason is that the cavities are inherently of molecular size, most often in polymer exhibiting considerably higher level of roughness that is difficult to be assessed by nanoscale imaging methods (AFM, SEM, etc.). That is especially true for peptide-imprinted polymers when only a characteristic short peptide chain of the parent protein is used as a template instead of the whole protein.

Therefore, we aimed to develop assisted methodologies for AFM to image the binding cavities and their surface density liberated after the template removal from peptide and protein-imprinted polymer nanofilms. Here, we are able to report on a new AFM methodology that can identify binding cavities after controlled gold deposition, and it can discriminate between the gold nanowires grown in the imprinted cavities and contingent unspecific gold deposition on the polymer surface (Figure 1). To validate our method, artificial "cavities" (holes) were generated by nanolithography and nanoindentation using AFM before the gold deposition. We determined the optimal gold deposition time and the hole size-dependency of gold growth.

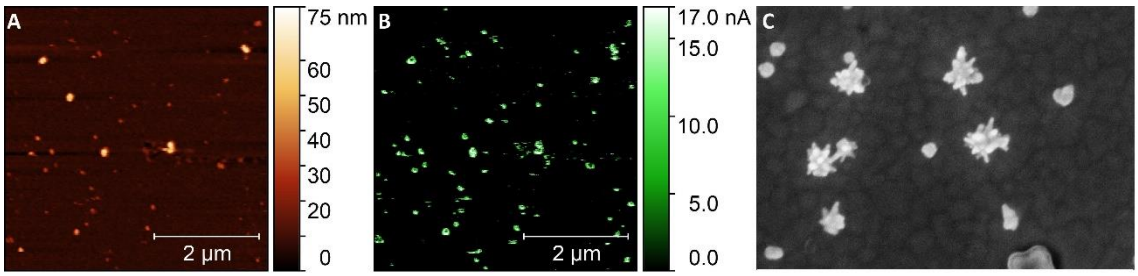

Figure 1. (A) Topography and (B) current map of a MIP after gold deposition.[2] (C) SEM image of gold growth on the polymer thin film.

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P13

Study of Soft Particles Fusion in the Presence of Surface Active Species at the Macroscopic Electrified Liquid-Liquid Interface

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In the electrochemistry community, ITIES is known as the interface between two immiscible electrolyte solutions or a polarized liquid-liquid interface. Thanks to its unique properties, it is defect-free, reproducible in terms of shape and molecular arrangements, and an easily renewable alternative to traditional solid electrode-based solutions. The ITIES finds application in various analytical areas, including the detection of (i) simple organic molecules, (ii) inorganic compounds, (iii) biochemicals such as DNA, proteins, and peptides, or (iv) illicit drugs. Additionally, ITIES has shown great potential in studying soft objects, so far, emulsion droplets and/or micelles. By utilizing ITIES, researchers can gain valuable insights into the behavior of these objects and their interactions with the soft junctions.[1–3]

Therefore, in this study, macro-ITIES was used to investigate the fusion of organic phase droplets suspended in the aqueous phase (oil-in-water emulsion) upon their contact with the soft interface. Three surface-active species were selected – cetyltrimethylammonium cation, sodium dodecyl sulfonate, and 1-tetradecanol to stabilize the emulsion and to ensure the droplets surface charge. Cyclic voltammetry was employed to investigate the behavior of selected surfactants at the ITIES. Electroanalytical data are supported by the critical micelle concentration values determined at the polarized liquid-liquid interface using the drop-shape analyzer. The core of this study was to define the effect of neutral and ionic surfactants that stabilize the colloidal solution on the electroanalytical output of the impact events. Therefore, chronoamperometry was employed to explore the behavior of the soft objects in their bare form, as well as when they were stabilized with surfactants.

Acknowledgments:
This work is supported by the National Science Centre of Poland (2021/43/O/ST4/01553).

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P14

Potential Driven $Ni(OH)_2$-Type Nanoparticle Preparation from Nickel Salen Polymers for Efficient Urea Electrocatalysis

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The presented study aimed at adjustment of preparation and regeneration conditions of $Ni(OH)_2$-type NPs embedded in the poly(SaltMe) and poly(*meso*-SaldMe) matrixes. Such prepared catalysts were employed in urea electrocatalysis. The proper treatment of urea-containing wastewater is essential from an environmental point of view. Disposing of untreated urea-rich wastewater can cause serious environmental problems because of its decomposition into ammonia and other nitrogen-based pollutants. Moreover, the activity, stability, and regeneration abilities of Ni-based catalysts are far from those requirements for commercialization. To tackle such problems, urea electrocatalysis oxidation operation conditions on previously tuned molecular structures of NPs embedded in poly(SaltMe) and poly(*meso*-SaldMe) were optimized.

For such optimization studies, we employed $Ni(OH)_2$-type NPs catalysts generated in 1 M $NaOH_{aq}$ from poly(NiSaltMe)[2] and poly(*meso*-NiSaldMe)[3] because transmission electron microscopy (TEM) and scanning electron microscopy (SEM) revealed that these catalysts nanostructure and arrangements of poly(Salen) matrixes were the most spatially diversified arranged pointing at facilitated access of urea to active sites.

In the final step, we studied the effect of the different $NaOH_{aq}$ concentrations during the catalytic oxidation of urea on the prepared catalysts to find out the $NaOH_{aq}$ concentration favoring the highest possible regeneration of the catalytic centers. For that, we tested our catalyst under cyclic voltammetry (CV) conditions in the presence of 0.3 M urea in the potential range of 0.0–1.0 V vs. Ag/AgCl in different $NaOH_{aq}$ concentrations. We chose the 0.3 M urea concentration because it is closer to its content in urine. Performed detailed studies indicated that electrocatalytic urea oxidation on both poly(NPs-$Ni(OH)_2$Salen) catalysts undergo the indirect EC' mechanism,[4] the so-called regeneration mechanism.[5] Moreover, CV experiments were conducted at different scan rates in the presence and absence of urea to identify electrochemical control conditions (diffusion or kinetic control).

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P15

Discrimination of Neutral and Sialylated Glycoproeins Modified with Osmium(VI) Complexes Using Square Wave Voltammetry

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Glycans, also those in glycoproteins, play a critical role in health and disease.[1] One of the building blocks of human glycans is *N*-acetyl-neuraminic acid, belonging to sialic acids (SA). SA are negatively charged monosaccharides usually located at the terminal position of glycan structures on the cell surface and secreted glycoconjugates. Abnormal sialylation was described for tumor growth, metastasis, as well as immune evasion. So, the amount and type of bound SA can be used for biorecognition in biosensors and could be of high therapeutic value. New methods for more specifically recognizing SA molecules, including the SA linkage on glycoconjugate, are still needed. Recently, we developed a simple and fast method based on glycan modification with osmium(VI) *N*,*N*,*N*',*N*'-tetramethylethylenediamine, [Os(VI)tem], followed by voltammetric detection at mercury electrodes.[2,3] Oligosaccharides (OLS)-Os(VI)tem products can be simply prepared by mixing the biomolecule with Os(VI)tem at room temperature. Then, unpurified Os(VI)tem-OLS is directly studied from the reaction mixture. In this work, we showed that neutral and sialylated OLSs, even those in glycoproteins, can be distinguished after their modification with Os(VI)tem complexes, also at graphite electrodes. Graphite electrodes are more suitable for sensing than mercury ones. These results could find practical applications in the analysis of glycoprotein biomarkers since the specificity of glycoprotein biomarkers can be significantly enhanced by analyzing their sugar components containing frequently different isomers.

Acknowledgments:
This research was supported by the Czech Science Foundation project No. 22-26590S.

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P16

Impact of Layer Thickness on Stability of Molecularly Imprinted Polypyrrole on the Indium Tin Oxide Modified Electrode

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Molecularly imprinted polymers (MIPs) are created by polymerizing functional monomers in the presence of template molecules, which are extracted after polymerization. This process forms cavities in the polymer matrix complementary to target molecules.[1] Different polymers and polymerization methods can be used to form MIPs. Conducting polymers such as polyaniline, polypyrrole, polythiophene, and poly(3,4-ethylenedioxythiophene) have consistently emerged as popular choices among conducting polymers for sensors and biosensors development. Polypyrrole has become a subject of particular interest in biosensor development due to its impressive electrical conductivity, ease of synthesis from water-based solutions, stability, and favorable mechanical properties, making it a promising choice for cost-effective and sensitive biosensors.[2,3]

In this study, the polypyrrole layer was electropolymerized on a glass/indium tin oxide electrode in the presence of a methylene blue. It has been observed that both too thick or too thin polymer layers can cause some difficulties in mechanical adhesion to the electrode surface.

Therefore, this research aimed to evaluate the stability of the different thickness polypyrrole layers on the electrode. The change in absorbance (ΔA) was used as an analytical signal.

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P17

Galectin-1 at the Charged Surfaces. Constant Current Chronopotentiometric Stripping Sensing

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Galectin-1 is a small lectin that belongs to a family of multifunctional lectins that play an important role in cell growth regulation, immunomodulation, cell signaling, angiogenesis, and neuroprotection.[1] Galectin-1 typically binds β-galactose-containing glycoconjugates in its carbohydrate-recognition domain.[2] However, the lectin interactions with natural ligands are relatively weak, which makes their study and detection challenging. Constant current chronopotentiometric stripping (CPS) is a label-free and highly structure-sensitive method commonly used for protein and/or peptide analysis. Both proteins and peptides yield so-called peak H due to catalytic hydrogen evolution reaction. In most cases, CPS is primarily used for measuring free proteins as well as strong interactions between them or with other molecules.[3] Nevertheless, in our last work, regarding lectin *Sambucus nigra* and its natural trisaccharide ligands,[4] we showed that with carefully selected parameters, it is possible to detect weak interactions as well.

In this work, we studied the interactions of galectin-1 with its natural ligands – D-lactose and *N*-acetyl-D-lactosamine. Compared to lectin *Sambucus nigra*, galectin-1 ligands are neutral, and their interaction is much weaker.

Acknowledgments:
This work was supported by the Czech Science Foundation project No. 23-06115S.

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P18

New Inorganic Nanocoatings for Antibacterial and Catalytical Applications

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Fully inorganic coatings show specific advantages over organic or hybrid materials. They are usually more stable and less prone to chemical leaching, allowing longevity and durability. There are known techniques for obtaining fully inorganic nanocoatings. Both physical methods (e.g., chemical or physical vapor deposition (CVD, PVD), laser ablation, atomic layer deposition (ALD), spray, spin, and dip-coating) and chemical methods (sol-gel, electrodeposition, hydrothermal synthesis) are not versatile enough to offer a single procedure to obtain a variety of different coatings on a variety of different substrates.

In previous works, we developed a method for creating a fully inorganic layer of nanocomposite consisting of nanoparticles embedded in the polyoxoborate matrix.[1] The method utilizes bare gold nanoparticles stabilized by borate anions. Borates polymerize upon acidification, creating inorganic nanocoatings consisting of metal nanoparticles in a polyoxoborate matrix. The process is eco-friendly as it is water-based, and nearly all suspended nanoparticles are deposited onto a substrate. Until now, we have demonstrated the advantages of gold-polyoxoborate coatings in biomedical applications and material sciences.[2,3] Our work now focuses on developing similar coatings using other metals as nanoparticle cores to broaden the method applicability.

Expanding a readily available nanomaterial coatings portfolio is an essential aspect of these studies. By introducing various metals, we can fine-tune the material coatings to a desired application and decrease the overall costs. Further investigation of other metals will open this technology for multiple fields in the future (such as optoelectronics, biology, medicine, and others).

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P19

A Study of Cytochrome bd in a Tethered Bilayer Lipid Membrane

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The rise in antibiotic resistance is a major current health concern. With the upsurge in multi-drug-resistant and extreme antibiotic-resistant strains, even fewer treatment options are available to treat bacterial infections.[1] In this search for novel antibiotic targets, the terminal oxidase cytochrome *bd* from *Mycobacterium tuberculosis* surfaced as a promising candidate. This transmembrane multi-heme respiratory enzyme couples the oxidation of quinols to the reduction of oxygen, thereby contributing to the formation of the proton motive force required for ATP synthesis. Cytochrome *bd* is predominantly used by bacteria under hostile conditions due to its high affinity for oxygen and high resistance against toxic compounds, which is highlighted in the indispensable nature of cytochrome *bd* under infectious conditions.[2] The study of cytochrome *bd*, however, proves challenging due to its hydrophobic nature and redundancy under lab culturing conditions.[3] This constrains most research on cytochrome *bd* in an unnatural detergent environment with truncated quinone analogs.

In this project, we study cytochrome *bd* in a native quinone/lipid environment and develop a novel drug screening method to aid in the search for new antibiotics. Consequently, we have expressed cytochrome *bd* from *Escherichia coli* and *Mycobacterium tuberculosis*, followed by reconstitution in proteoliposomes. The activity of the cytochrome *bd* was studied via oxygen consumption on a Clark-type electrode and cyclic voltammetry in a tethered-bilayer lipid membrane (tBLM) system. This tBLM system was prepared by depositing a lipid bilayer on a cholesterol-modified template-stripped gold electrode, enabling electron transfer between the gold surface and the membrane-embedded quinones. Combining these methods allows for comparing different quinone subtypes, truncated analogs, and inhibitors.

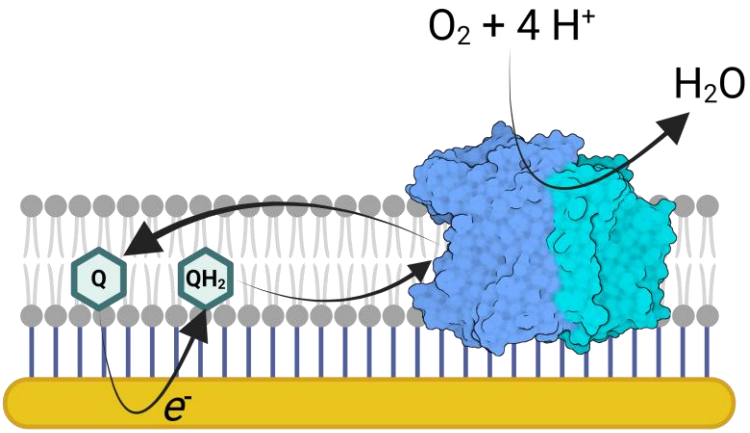

Figure 1. Catalytic activity of cytochrome *bd* in a tethered bilayer lipid membrane system. Figure created with Biorender.

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See you all
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Photography: Dominik Korol

Chief Editor of the Book of Abstracts
Dominik Korol
Institute of Physical Chemistry, Polish Academy of Sciences
Warsaw, Poland
Published: October 2023

ISBN 978-83-939295-5-9