# CROSSNANO
# CROSSBORDER WORKSHOP IN NANOSCIENCE AND NANOTECHNOLOGY

## WHEN

22-24 February 2022
9:00 – 18:00

## WHERE

Room 3B, Building H3
University of Trieste
and
on line
via Microsoft Teams

PhD School in Nanotechnology

**UNIVERSITY OF TRIESTE**

## ORGANIZERS

University of Trieste

Jožef Stefan International Postgraduate School

Jožef Stefan Institute

University of Ljubljana

# 2nd CrossNano Workshop

**Crossborder Workshop in Nanotechnology and Nanoscience**
February 22–24, 2022
University of Trieste, Room 3B, Building H3 and on-line

**In cooperation with**
Jožef Stefan International Postgraduate School, Ljubljana, Slovenia
Jožef Stefan Institute, Ljubljana, Slovenia
University of Ljubljana (Faculty of Mathematics and Physics, Faculty of Pharmacy, Faculty of Electrical Engineering), Ljubljana, Slovenia

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Prof. Dragan Mihailović, Prof. Darja Lisjak and Dr. Alenka Mertelj,
*Jožef Stefan International Postgraduate School, Jožef Stefan Institute, University of Ljubljana*

**Technical Support:** Paola Posocco, *University of Trieste*

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"FERNANDO TOMMASINI" and "ALESSANDRO DE VITA" AWARD: Albano Cossaro, Slavko Kralj, Darja Lisjak, Vanni Lughi, Alenka Mertelj, Alberto Morgante, Jelena Papan, Paola Posocco
"BEST CAREER" AWARD: Albano Cossaro, Lucia Pasquato, Paola Posocco

**Edited by**: Darja Lisjak, Paola Posocco, Dragan Mihailović and Alberto Morgante

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MEDNARODNA PODIPLOMSKA ŠOLA JOŽEFA STEFANA
JOŽEF STEFAN INTERNATIONAL POSTGRADUATE SCHOOL

Jožef Stefan Institute
Ljubljana, Slovenija

University *of Ljubljana*

# FEBRUARY 22

**9:00-9:30** **OPENING**
**Alberto Morgante** – *Coordinator of the PhD School in Nanotechnology, University of Trieste*
**Alessandro Baraldi** – *Delegate for Research and PhD of the University of Trieste*

**CHAIR: Alberto Morgante**

| | PhD student | Cycle | Supervisor | Title |
|---|---|---|---|---|
| **9:30-9:50** | Beatrice Bartolomei | 36 | M. Prato | Nuclear magnetic resonance discloses flaws in carbon nanodot samples |
| **9:50-10:10** | Nicoletta Braidotti | 36 | D. Cojoc | Near-interface investigation of cytoskeletal drugs' effect on cells' rheological response |
| **10:10-10:30** | Valeria Chesnyak | 36 | C. Africh | Carbide coating on nickel to enhance the stability of supported metal nanoclusters |
| **10:30-10:50** | Deepak Dagur* | 36 | P. Torelli | Light induced magnetic modifications in multiferroic heterostructures |
| **10:50-11:10** | Žiga Ponikvar* | - | S. Gyergyek | Methods of catalyst preparation for ammonia decomposition |

**11:10-11:30** **BREAK**

**CHAIR: Tomaž Mertelj**

| | PhD student | Cycle | Supervisor | Title |
|---|---|---|---|---|
| **11:30-11:50** | Farooq Ayesha | 36 | S. Fabris | Development of high-strength nanostructured multilayers for applications in nuclear fusion reactors |
| **11:50-12:10** | Veronika Kost | 36 | T. Da Ros | Preparation of BN graphene quantum dots and investigation of their photophysical and electrochromic properties |
| **12:10-12:30** | Claudio Lentini Campallegio | 36 | A. Morgante | Charge dynamics in complex 2D heterostructures |
| **12:30-12:50** | Carolina Paba | 36 | L. Casalis | Biophysical analysis of small extracellular vesicles (sEVs) and their interaction with model plasma membrane |
| **12:50-13:10** | Jernej Ekar* | - | J. Kovač | Reduction of matrix effect in ToF-SIMS depth profiling via $H_2$ flooding |

**13:10-15:10** **BREAK**

**CHAIR: Lucia Pasquato**

| | PhD student | Cycle | Supervisor | Title |
|---|---|---|---|---|
| **15:10-15:30** | Giulia Della Pelle* | - | N. Kostevšek | Erythrocyte-derived carriers for theranostics applications |
| **15:30-15:50** | Petr Rozhin | 36 | S. Marchesan | Towards composite hydrogels with functionalized carbon nanostructures and a self-assembling tripeptide |
| **15:50-16:10** | Smritirekha Talukdar | 36 | T. Montini | Reduction of $CO_2$ to fuels by photocatalysis and electrocatalysis |

| | | | | |
|---|---|---|---|---|
| **16:10-16:30** | Spase Stojanov* | - | A. Berlec | Incorporation of vaginal lactobacilli into electrospun nanofibers: toward a new treatment of vaginal infections |
| **16:30-16:50** | Martina Zangari | 36 | L. Vaccari | On the role played by protein-asbestos fiber interaction in asbestos toxicity: a multi-technique approach from single fiber to cellular and tissue milieu |
| **16:50-17:10** | Federica Zingaro | 36 | G. Gianoncelli | Toxicological research: labelled microplastics detection in an *in vitro* human model by soft X-Ray micro-spectroscopy |

*online talk.

# FEBRUARY 23

**CHAIR: Albano Cossaro**

| | PhD student | Cycle | Supervisor | Title |
|---|---|---|---|---|
| **09:30-9:50** | Matteo Bisetto | 35 | P. Fornasiero | A study inside the catalytic behavior of $Cu_2O$ nanoparticles |
| **09:50-10:10** | Mario Daka | 34 | L. Pasquato | Reduced polynuclear Pd8 complex for heterogeneous Suzuki-Miyaura cross-coupling reactions |
| **10:10-10:30** | Matteo Cretella | 35 | L. Pasquato | Design, synthesis and use of organic-inorganic nanoparticles protected by fluorinated ligands as nanomaterial for imaging and therapy |
| **10:30-10:50** | Magdhi Kirti | 35 | G. Biasiol | Optimization of semiconductor-superconductor nano-systems for the development of Andreev qubits |
| **10:50-11:10** | Yevhenii Vaskivskyi* | - | D. Mihailović | Chiral domains and charge density wave dynamics in $1T\text{-}TaS_2$ |
| **11:10-11:30** | **BREAK** | | | |

**CHAIR: Alenka Mertelj**

| | PhD student | Cycle | Supervisor | Title |
|---|---|---|---|---|
| **11:30-11:50** | Federico Loi | 35 | A. Baraldi | The smallest silver oxide |
| **11:50-12:10** | Silvia Mauri* | 35 | P. Torelli | Investigation of the surface reactivity of catalysts by operando X-ray absorption spectroscopy with synchrotron radiation |
| **12:10-12:30** | Edoardo Raciti | 35 | M. Prato | Defect-modulated catalytic response in 2D carbon nitride: insights from modeling |
| **12:30-12:50** | Luka Pavešič* | - | R. Žitko | Subgap states in superconducting islands |
| **12:50-14:50** | **LUNCH** | | | |

**CHAIR: Darja Lisjak**

| | PhD student | Cycle | Supervisor | Title |
|---|---|---|---|---|
| **14:50-15:10** | Aharon Steffè | 35 | G. Toffoli | Triple-action nanoplatform for theranostic applications in hepatocellular carcinoma (HCC) |
| **15:10-15:30** | Mina Taleblou | 35 | S. Piccinin | Study of CO oxidation on Pt atomic systems supported on TiO2 |
| **15:30-15:50** | Michele Zanetti* | 35 | M. Lazzarino | Cardiac tissue models to investigate the heart mechanobiology |
| **15:50-16:10** | Marco Beltrami | 34 | O. Sbaizero | Nanostructured multilayer coatings for wood cutting tools |
| **16:10-16:30** | **BREAK** | | | |

**CHAIR: Alois Bonifacio**

| | PhD student | Cycle | Supervisor | Title |
|---|---|---|---|---|
| **16:30-16:50** | Erik Betz-Güttner | 34 | M. Lazzarino | Terahertz sensing with Golay cell microarray device |

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|---|---|---|---|---|
| **16:50-17:10** | Davide Busato | 34 | G. Toffoli | Antibody-driven chitosan nanoparticles for drug delivery strategies in pancreatic ductal adenocarcinoma |
| **17:10-17:30** | Martina Conti | 34 | M. Lazzarino | Nanomechanical sensors in partial wetting condition for biosensing application |

*online talk.

# FEBRUARY 24

**CHAIR: Vanni Lughi**

| | PhD student | Cycle | Supervisor | Title |
|---|---|---|---|---|
| **9:30-9:50** | Filippo Costa | 35 | S. Prato | Imaging and analysis at nanoscale. Merging between SPM and optics |
| **9:50-10:10** | Federica Di Cintio* | 34 | G. Toffoli | Nanoparticles anti-GPC1 for glioblastoma multiforme treatment |
| **10:10-10:30** | Simone Di Noja* | 34 | M. Prato | Transfer of axial chirality to the nanoscale endows carbon nanodots with circularly polarized luminescence |
| **10:30-10:50** | Dževad K. Kozlica* | - | I. Milošev | Characterization of the localized corrosion phenomena of Al/Cu galvanic couple by scanning electrochemical microscopy |
| **10:50-11:10** | **BREAK** | | | |

**CHAIR: Francesca Larese Filon**

| | PhD student | Cycle | Supervisor | Title |
|---|---|---|---|---|
| **11:10-11:30** | Alessandro Esposito | 34 | V. Sergo | Label-free SERS spectroscopy new perspectives in the bioanalytical field and biofluids analysis |
| **11:30-11:50** | Marcello Ferrara* | 34 | P. Fornasiero | Effects of $SO_2$ trace impurities in $CO_2$ feed on copper and Tin based catalysts during $CO_2$RR |
| **11:50-12:10** | Arianna Gazzi | 34 | M. Prato | Immunocompatibility and biomedical applications of new nanomaterials |
| **12:10-12:30** | Uroš Hribar* | - | J. König | Direct foaming of CRT waste glass in air atmosphere |
| **12:30-12:50** | Matjaž Dlouhy* | - | A. Kokalj | How adsorbed H, O, OH, and Cl affect on the adsorption of imidazole on copper |
| **12:50-14:50** | **LUNCH** | | | |

**CHAIR: Serena Bonin**

| | PhD student | Cycle | Supervisor | Title |
|---|---|---|---|---|
| **14:50-15:10** | Monica Mossenta | 34 | G. Toffoli | Set-up of anti-GPC3-driven polymeric nanoparticles in hepatocellular carcinoma |
| **15:10-15:30** | Lorenzo D'Amico | 36 | G. Tromba | Imaging and characterization of fibrotic tissues |
| **15:30-15:50** | Cristian Soncini | 34 | M. Pedio | The influence of molecular ordering on the cobalt phthalocyanine excited states dynamics |
| **15:50-16:10** | **BREAK** | | | |
| **16:10-16:30** | **"FERNANDO TOMMASINI" AWARD**<br>**"ALESSANDRO DE VITA" AWARD**<br>**"BEST CAREER" AWARD** | | | |
| **16:30-16:40** | **CLOSING REMARKS** | | | |

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|---|---|
| | **Alberto Morgante** – *Coordinator of the PhD School in Nanotechnology, University of Trieste*<br>**Dragan Mihailović** – *Director of the Centre of Excellence in Nanoscience and Nanotechnology (Ljubljana), Institut Jožef Stefan and University of Ljubljana* |

*online talk.

# Gold nanoparticles decorated with customized self-assembled monolayers: a versatile platform toward the development of nano-biosensors

Ahmed Alsadig,[1*] Hendrik Vondracek,[2] Paolo Pengo,[3] Lucia Pasquato,[3] Sara Fortuna,[3] Paola Posocco,[4] Pietro Parisse[2] and Loredana Casalis[2]

*ahmed.mohammed@elettra.eu

[1] *Department of Physics, University of Trieste, Piazzale Europa 1, 34127 Trieste, Italy*
[2] *NanoInnovation Lab, Elettra-Sincrotrone Trieste S.C.p.A., 34149 Basovizza, Trieste, Italy*
[3] *Department of Chemical and Pharmaceutical Sciences, University of Trieste, via Licio Giorgieri 1, 34127 Trieste, Italy*
[4] *Department of Engineering and Architecture, University of Trieste, via Valerio 17, 34127 Trieste, Italy*

The self-organization of ligands at the surface of metallic nanoparticles gives rise to the construction of medical diagnostics platforms with advanced merits. In our lab, we exploited an approach based on the DNA-directed immobilization of protein-DNA conjugates onto a mixed self-assembled monolayer (mixed-SAM) composed of thiolated ssDNA and oligo ethylene glycols-terminated alkylthiols with the possibility to adjust DNA density to the steric size of the protein of interest.[1] This design methodology is general and represents a promising tool for anchoring and detecting various biomolecules. Besides, a simple, label-free, and rapid approach to quantify Trastuzumab, a humanized IgG1 monoclonal antibody used against HER2 positive cancer, based on localized surface plasmon resonance (LSPR) was developed.[2] We demonstrated the capability for detecting clinically relevant concentrations of Trastuzumab down to 300 ng/ml in the buffer and 2 µg/ml in diluted serum. This strategy was found to be fast, and highly specific to Trastuzumab. To circumvent the limitation encountered when working in complex, non-purified biological fluids, a click chemistry protocol based on alkyne SAMs and azide-modified biomolecules are currently being implemented in our lab.

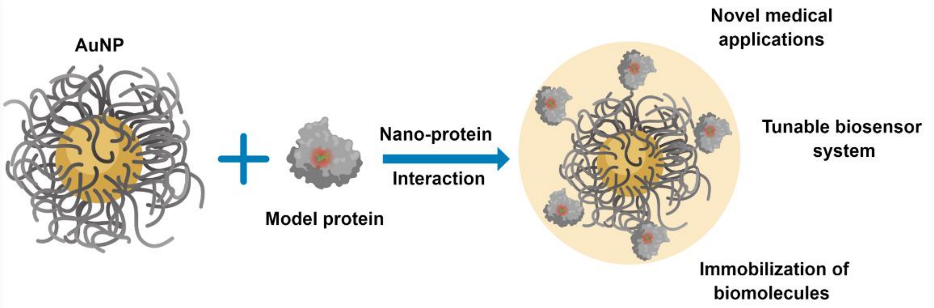


Figure 1. Various gold nanoparticle bio-functionalization routes are exploited and adapted to diverse needs.

**Acknowledgements**: We are grateful to Structural Biology Laboratory at Elettra Sincrotrone Trieste for the facility and technical support.

(1) J. Deka et al. ACS Applied Materials & Interfaces 2015, 7, 7033-7040.
(2) A. Alsadig et al. Nanomaterials 2021, 11, 3181.

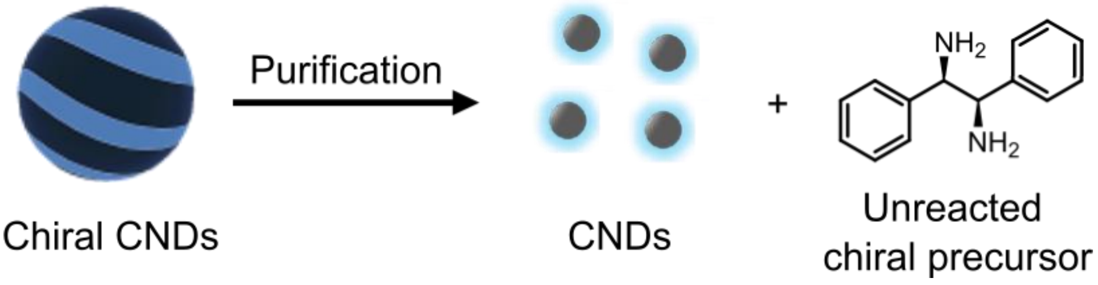
# Nuclear magnetic resonance discloses flaws in carbon nanodot samples

Beatrice Bartolomei,[1] Andrea Bogo,[1] Francesco Amato,[1] Giulio Ragazzon[1,2] and Maurizio Prato[1,3,4*]

*prato@units.it

*[1] Department of Chemical and Pharmaceutical Sciences, INSTM UdR Trieste, University of Trieste, via Licio Giorgieri 1, 34127 Trieste, Italy*
*[2] Institut de Science et d'Ingénierie Supramoléculaires, University of Strasbourg, 8 allée Gaspard Monge, 67000, Strasbourg, France*
*[3] Centre for Cooperative Research in Biomaterials (CIC BiomaGUNE), Basque Research and Technology Alliance (BRTA), Paseo de Miramón 194, 20014, Donostia San Sebastián, Spain*
*[4] Basque Fdn Sci, Ikerbasque, 48013 Bilbao, Spain*

Carbon nanodots are currently one of the hot topics in the nanomaterials world, due to their accessible synthesis and promising features.[1–3] However, the purification of these materials is still a critical aspect, especially for syntheses involving molecular precursors. Indeed, the presence of unreacted species or small organic molecules formed during solvothermal treatments can affect the properties of the synthesized nanomaterials.[4,5] Key to identify molecular species in carbon nanodot samples is the use of nuclear magnetic resonance. In our work, we have investigated two case-studies in which nuclear magnetic resonance analysis was used to reveal that the chiral and emissive properties of different type of carbon nanodots arise from molecular species rather than from carbon nanoparticles.



(1) A. Sciortino, et al. C 2018, 4, 67.
(2) S. N. Baker et al. Angew. Chem. Int. Ed. 2010, 49, 6726–6744.
(3) F. Arcudi et al. Angew. Chem. Int. Ed. 2016, 55, 2107–2112.
(4) Y. Xiong et al. Nano Today 2018, 23, 124–139.
(5) W. Kasprzyk et al. Nanoscale 2018, 10, 13889–13894.

# Nanostructured multilayer coatings for wood cutting tools

Marco Beltrami,[1,2*] Simone Dal Zilio,[2] Marco Lazzarino[2] and Orfeo Sbaizero[1]

*marco.beltrami@phd.units.it

[1] *Department of Engineering and Architecture, University of Trieste, 34127 Trieste (TS), Italy*
[2] *CNR-IOM, Istituto Officina dei Materiali - Consiglio Nazionale delle Ricerche, 34149 Trieste (TS), Italy*

Cutting tools are an important factor in the economy of many industrial manufacturing industries, such as automotive, aerospace and wood industries. The lifetime of such tools is limited by progressive deterioration of the cutting edge due to the harsh machining conditions. Eventually, this results in lower surface finishing, increased power consumption, need of parts replacement and, therefore, lower productivity.[1] To extend their service life, cutting tools are usually protected with hard and refractory Transition Metal Nitrides (TMNs) coatings with single- or multi-layer architecture.[2] Nanostructured Multilayer Coatings (NMCs) consist in an alternating structure of two constituent materials. This alternated architecture delivers several benefits to the coating performance such as higher design flexibility and improved mechanical properties and corrosion resistance. Nonetheless, in wood machining, the concomitant occurrence of high cutting temperatures, corrosive and abrasive agents, strict technical cutting requirements and 3D anisotropy of wood-based materials have strongly limited the industrial and commercial diffusion of coated tools.[3] NMCs based on PVD-deposited corrosion-resistant Chromium Nitride (CrN) and hard Tungsten Nitride (WN) are being studied in respect to their structural, mechanical, and electrochemical properties to exploit the high corrosion resistance of CrN and the improved mechanical properties delivered by hard WN. Preliminary results suggest that nanostructured multilayer systems with individual layer thickness of a few to tens of nanometers have higher protective properties than monolayer coatings. Indeed, higher mechanical properties, corrosion resistance and structural-topographical features have been observed for progressively thinner constituent layers thickness. Finally, a study on the roughness build-up during multilayers deposition is proposed and discussed in terms of the energetics involved in the deposition processes of the two constituent materials.

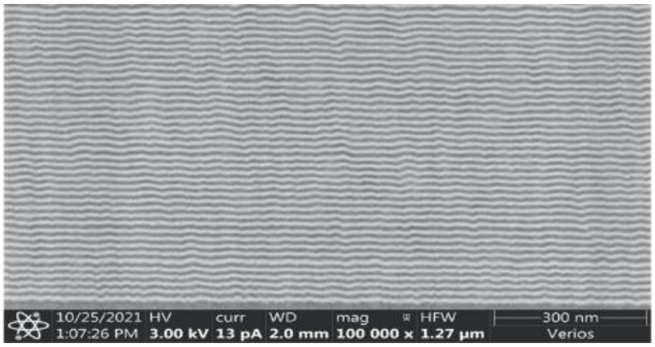


Figure 1: SEM cross-section image of a CrWN multilayer coating with 10 nm-per-layer architecture.

**Acknowledgements:** The research is founded by the European NANO-REGION project under the Interreg ITA-SLO program and developed in cooperation with project-partners from the University of Nova Gorica, the Jozef-Stefan Institute of Ljubljana and University Ca 'Foscari of Venice.

(1) J. Karandikar et al., Int. J. Adv. Manuf. Technol. 2015, 77, 021082001.
(2) A. Pogrebnjak et al., Coatings 2019, 9, 9030155.
(3) B. Kucharska et al., Materials 2021, 14, 14112740.

# Terahertz sensing with Golay cell microarray device

Erik Betz-Güttner,[1,2*] Simone Dal Zilio[2] and Marco Lazzarino[2]

*erik.betzguttner@phd.units.it

*[1] Department of Physics, University of Trieste, Piazzale Europa 1, 34127 Trieste, Italy*
*[2] CNR-IOM, Istituto Officina dei Materiali - Consiglio Nazionale delle Ricerche, 34149 Trieste (TS), Italy*

The THz radiation is a part of the electromagnetic spectrum between microwaves and infrared. When described as made of photons, their quantum of energy is lower than $k_BT$ at room temperature, and the strategies used in photon detection cannot be applied. When described in terms of high-frequency EM waves, the associated electron velocity in a material is faster than any known material. So the strategies used to generate or detect the radiofrequency cannot be applied. Hence, the use of the term THz gap to denote the lack of resources in a field that has otherwise many potential applications.[1] Among the incoherent detectors commercially available in the market, the Golay cell is one of the most sensitive thermal detectors, however, its design remained practically unchanged since its invention in 1947.[2] The advent of new technologies and materials like graphene could allow the breakthrough needed to innovate this detector and partially close the gap. Unfortunately, many practical limitations like the brittleness of suspended monolayer graphene, hindered its development towards application on the microscale[3]. This work aimed at developing a method capable of overcoming these problems resulting in the efficient sealing and enclosure of an array of micrometre-scale cells with an ultrathin membrane. The membrane was composed of CVD single-layer graphene and a reinforcing nm-thin titanium layer and efficiently combined the strength of a monoatomic layer of carbon and the toughness of an ultrathin metal layer. A back-side sealing was provided by a silicone rubber cork: the two-side sealing allows the transfer of mm-sized membranes avoiding the problems arising during the membrane wet-transfer from an aqueous solution. Additionally, the silicone provided a simple and re-usable sealing allowing the change of the material sealed in the cells. Finally, these water- and gas-tight sealed arrays were tested under the irradiation coming from a filtered Globar source and promptly responded proving their potential as Golay cells by detecting the THz radiation.

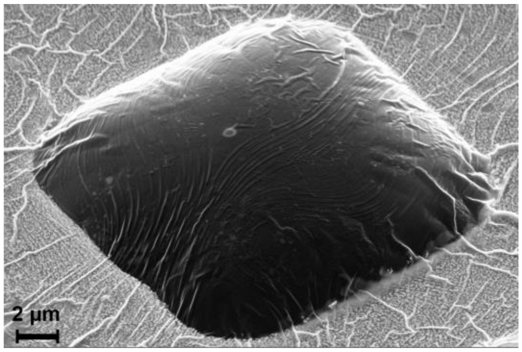


Figure 1. Example of a continuous, fully sealed Ti/Gr membrane with 10 nm of Ti forming a Golay cell. The membrane is able to withstand the pressure difference in the SEM (1 bar) proving its potential as a strong sealing membrane over large, suspended areas.

**Acknowledgements**: The authors would like to thank the ATTRACT project "GRANT" and the Interreg V-A Italy-Slovenia 2014-2020 strategic project "NANO_REGION" for the financial support.

(1) A. Y. Pawar et al., Drug Invention Today 2013, 5, 157–163.
(2) M. J. E. Golay, Rev. Sci. Instrum. 1947, 18, 357–362.
(3) P. Zhang et al., Nat. Commun. 2014, 5, 3782.

# A study inside the catalytic behavior of $Cu_2O$ nanoparticles

Matteo Bisetto,[1] Alberto Naldoni,[2,3] Tiziano Montini[1] and Paolo Fornasiero[1]

matteo.bisetto@phd.units.it

[1]*Department of Chemical and Pharmaceutical Sciences, ICCOM-CNR Trieste, INSTM-Trieste, Università di Trieste, Via L. Giorgieri 1, 34127 Trieste, Italia*
[2] *Regional Centre of Advanced Technologies and Materials, Faculty of Science, Palacký University, Šlechtitelů 27, 78371 Olomouc, Czech Republic*
[3] *Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu 610054, China*

In these years, different studies have reported the importance of nanostructuration to tailor the morphology at nanoscale and improve the overall performances of a material.[1,2] Due to the different coordination on the surface, well-defined nanocrystals show peculiar facet-dependent properties including different selectivity, anisotropic reactivity or stability. In particular, well-facet cuprous oxide ($Cu_2O$) nanocrystals got huge attention due to their unique facet dependent properties.[3] Being cheap and earth abundant, such well-defined $Cu_2O$ nanostructures can be used for different photocatalytic reactions thank to their strong visible light absorption coefficient. However, the low conversion efficiency and the poor photostability of $Cu_2O$ limits the industrial application of this material. In this project, pristine $Cu_2O$ nanoparticles ($Cu_2O$ NPs) with a tailored shape had been synthetized via a wet-chemical route. Two structures were chosen: cubic (CU-$Cu_2O$) and rhombic dodecahedra nanoparticles (RD $Cu_2O$). Different efforts were focused on the formation of different composites with $Cu_2O$ and the study of their catalytic properties. Formation of heterojunctions is one of the main solutions to contrast the very low stability of cuprous oxide and simultaneously, to enhance the photocatalytic properties of the material. Indeed, one of the main problems of $Cu_2O$ is the self-oxidation that occur when holes are photo-generated during a catalytic process.[4] In order to overcome this issue, different hybrid $Cu_2O$-based nanostructures were developed to enhance the photocatalytic activity by concomitantly increasing also the electron-hole separation efficiency. In particular, cuprous oxide had been coupled with nanostructured photocatalysts such as $C_3N_4$, $WO_3$ and $MoS_2$. The pristine materials and the different composites were also studied toward the electrocatalytic reduction of $CO_2$. With our home-made system it is possible to connect a gas-tight electrochemical cell to a potentiostat workstation and a GC in order to directly analyze the gaseous product of the reaction. Qualitative characterization of various samples evidences the formation of different products such as hydrogen, carbon monoxide, methane, formate and traces of alcohols. Moreover, a protocol had been developed in order to perform a quantitative characterization of the materials, in terms of conversion rates and faradaic efficiencies of the different products.

(1) S. Bai et al., Adv. Sci. 2017, 4, 1600216.
(2) S. Sun et al., Nanoscale 2019, 11, 15739–15762.
(3) K.C. Christoforidis et al., ChemCatChem 2019, *11*, 368–382.
(4) S. Rej et al., J. Mater. Chem. A 2021, 9, 5915-5951.

# Near-interface investigation of cytoskeletal drugs' effect on cells' rheological response

Nicoletta Braidotti[1,2]

*nicoletta.braidotti@phd.units.it

[1] *Department of Physics, University of Trieste, Via A. Valerio 2, 34127 Trieste, Italy*
[2] *Istituto Officina dei Materiali (IOM), Consiglio Nazionale delle Ricerche (CNR), Area Science Park-Basovizza, Strada Statale 14, km 163,5, 34149 Trieste, Italy*

In the field of cardiomyopathies, which represents an extremely important health problem, the alterations of the cell's cytoskeleton were found to be at the origin of most of these diseases.[1] The cytoskeleton, in fact, is a vital component of the cells, which imparts them rigidity and elasticity and thus the ability to react under external stimuli. In order to investigate how cell's mechanical properties are regulated as a consequence of these alterations, we used Cytochalasin D (Cyt-D) 5 µM and Nocodazole (Noc) 10 µM as depolymerizing agents for two main cytoskeletal elements: actin filaments and microtubules. We adapted and applied two complementary techniques for monitoring rheological and morphological variations of primary cardiac fibroblasts: Quartz Crystal Microbalance (QCM) and Digital Holographic Microscopy (DHM).[2, 3]

QCM was employed for studying the viscoelastic properties' variations within a nanometric layer upon the oscillating quartz surface. Due to complications related to the use of QCM with non-homogeneous viscoelastic films such are cells, the qualitative interpretations were discussed and supported by exploiting the quantitative analysis of morphological parameters (area, volume and cell thickness) provided by DHM. We observed a very fast Cyt-D effect which led to the loss of cell viscosity, cell rounding, loss of adhesion and detachment from the surface with a major effect observable within the first 10 minutes of treatment. Noc resulted, instead, to have a more progressive effect on cells with a continuous variation in rheological behavior during 4 hours of treatment. The higher vibrational energy's dissipation of the oscillating quartz observed in Noc reflects the cell's ability to maintain a firmly attachment to the substrate while the cytoskeletal rearrangement takes place. In fact, even if changes in shape were observed in Noc-treated cells by optical microscopy, the redistribution of the surface projected area led to a constant trend in the quantitative morphological measurements. In order to confirm the rate of drugs' action and the effect on cytoskeleton, immunofluorescence was performed against actin and tubulin. Cyt-D led to a rapid (10 min) depolymerization of F-actin in G-actin monomers without additional effects at prolonged drug exposure. Instead, Noc led to a less rapid (30 min) redistribution of tubulin through the cytosol. The completely disaggregation of filaments was observed at prolonged drug treatment where the compensatory effect of actin polymerization emerged with increased stress fibers formation, known to be a marker of fibroblasts phenoconversion to fibrosis' precursors: myofibroblasts.[4]

**Acknowledgements**: We acknowledge and thank the Italian Liver Foundation (Fondazione Italiana Fegato ONLUS, Trieste) for the donation of the excess animal tissues.

(1) A. J. Marian et al., Wehrens, Cardiovascular Research 2020, 116, 1600-1619.
(2) J. Y. Chen et al., Biosensor and Bioelectronics 2018, 99, 593-602.
(3) P. Marquet et al., Encyclopedia of Neuroscience 2009, 1, 675-683.
(4) N. Sandbo et al., The Journal of Biological Chemistry 2013, 288, 15466-15473.

# Antibody-driven chitosan nanoparticles for drug delivery strategies in pancreatic ductal adenocarcinoma

Davide Busato,[1,3*] Monica Mossenta,[1,3] Sara Capolla,[1,3] Monica Argenziario,[2] Federica Di Cinito,[1,3]
Aharon Steffè,[1,3] Roberta Cavalli,[2] Paolo Macor,[1] Michele Dal Bo[3] and Giuseppe Toffoli[3]

*davide.busato@phd.units.it

[1] *Department of Life Sciences, University of Trieste, Trieste, Italy*
[2] *Department of Pharmaceutical Sciences and Technology, University of Turin, Turin, Italy*
[3] *Experimental and Clinical Pharmacology Unit, Centro di Riferimento Oncologico (CRO), IRCCS , Aviano (PN) , Italy*

Pancreatic ductal adenocarcinoma (PDAC) causes more than 330,000 deaths every year worldwide.[1] In the majority of the cases the diagnosis occurs in an advantage stage, furthermore, this pathology is very resistant to chemotherapy.[2] The aim of the project is to set up a drug delivery strategy based on chitosan nanoparticles (CS-NPs) conjugated with a custom monoclonal antibody (C) against the specific PDAC antigen, Glypican 1 (GPC1). The project started with an identification and *in-vitro* evaluation of GPC1 as a specific PDAC antigen. Starting from three hybridomas we *in-vitro* evaluate the three monoclonal antibodies and we select the most specific one, called C, to bind on the NPs surface. The antibody C was *in-vivo* tested on a murine model harboring a subcutaneous model of PDAC and showed a high grade of affinity for PDAC cell line (BXPC3). CS-NPs, with a diameter of 360 nm and a positive zeta potential, were *in-vitro* evaluated on a BXPC3 to test their biocompatibility, the results demonstrated a high grade of biocompatibility. Taken together these results suggest the possibility to bind the antibody C on the NPs surface to evaluate the biodistribution of this nanotechnological device in-vivo. The biodistribution of CS-NPs was compared with CS-NPs-C in a murine model subcutaneous injected with BXPC3. The results highlighted the crucial role of C in the tumor delivery of the NPs since the level of tumor accumulation is higher in the case of CS-NPs-C. These results suggest a possible clinical involvement of this nanotechnological proposal in the clinical management of PDAC patients.

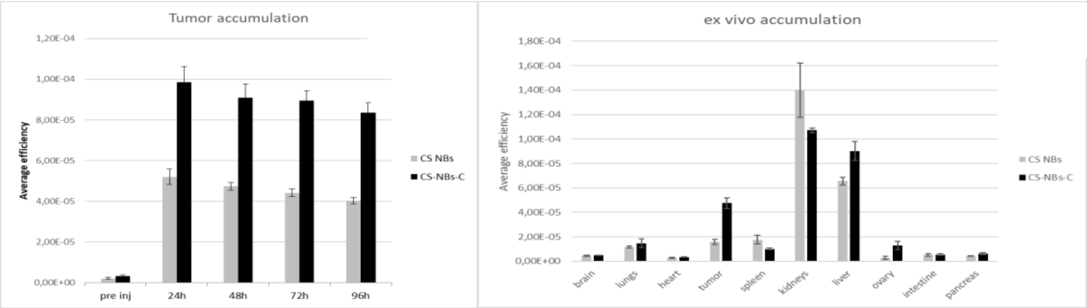


Figure 1. A: In-vivo tumor accumulation of CS-NBs and CS-NBs-C; B: Ex-vivo biodistribution of CS-NBs and CS-NBs-C.

**Acknowledgements**: I would like to thank all the members of Nanomedicine lab, Paolo Macor, Michele Dal Bo, and Giuseppe Toffoli.

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# Carbide coating on nickel to enhance the stability of supported metal nanoclusters

Valeria Chesnyak,[1,2]* Srdjan Stavrić,[1,3] Mirco Panighel,[2] Maria Peressi,[1] Giovanni Comelli[1,2] and Cristina Africh[2]

*chesnyak@iom.cnr.it

[1] *Physics Department, University of Trieste, via A. Valerio 2, Trieste 34127, Italy*
[2] *CNR-IOM, Laboratorio TASC, S.S. 14 Km 163.5, Basovizza, Trieste, 34149, Italy*
[3] *Vinča Institute of Nuclear Sciences - National Institute of the Republic of Serbia, University of Belgrade, P. O. Box 522, RS-11001 Belgrade, Serbia*

Co nanostructures are of high interest due to potential application in nanoscience e.g., as magnetic storage devices or heterogeneous catalysts. However, controlling the stability, shape and activity of these nanostructures is a major challenge. In this study, we characterize the structure and stability of metallic Co on bare Ni(100) and Ni-Carbide ($Ni_2C$) by means of variable temperature scanning tunneling microscopy complemented by DFT calculations. Deposition of 0.1 ML (monolayer) of Co leads to different nanostructures on bare Ni(100) and on $Ni_2C$ surface. In the case of bare Ni, Co forms randomly distributed, small (<5 nm diameter) islands of one-atomic-layer height. On Ni-carbide, bigger and higher islands of irregular shape form. Furthermore, unlike bare Ni, a step decoration is observed on $Ni_2C$. The thermal stability of Co on both surfaces was investigated by annealing in the STM stage up to 500 °C. In both cases, Co dissolution into the bulk was observed, although starting earlier and proceeding faster in case of the bare Ni substrate.

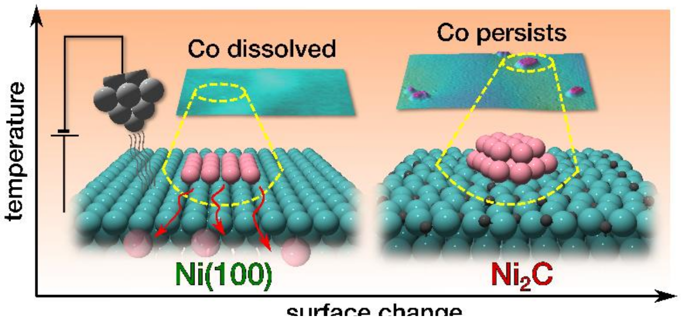

Figure 1. Co nanostructures show a higher thermal stability on Ni-carbide compared to a bare Ni surface.

To better understand the experimental results, theoretical calculations were performed in collaboration with Dr. Srdjan Stavrić and Prof. Maria Peressi (University of Trieste). The adsorption energies of Co adatoms and clusters up to a size of 25 atoms, as well as diffusion barriers on the two surfaces, were calculated and compared, confirming a higher stability of Co on $Ni_2C$ with respect to bare Ni. To support the experimental observations on the thermal stability and dissolution of Co, the penetration barrier of Co on both surfaces and the stability of substitutional Co in the first few surface layers were calculated and the dissolution process explained as a vacancy assisted process.

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# Nanomechanical sensors in partial wetting condition for biosensing application

Martina Conti,[1,2] Laura Andolfi,[2] Erik Betz-Güttner,[1,2] Simone Dal Zilio[2] and Marco Lazzarino[2]

*martina.conti@phd.units.it

*[1] Department of Physics, University of Trieste, 34100 Trieste, Italy*
*[2] Istituto Officina dei Materiali-Consiglio Nazionale delle Ricerche (IOM-CNR), Basovizza, 34149 Trieste, Italy*

Recent studies have shown how commercial cantilevers can be used as nanomotion sensors to convert the small movements of living cells into dynamic oscillations.[1] The application of nanomechanical sensors in biology requires operating in a liquid environment, which affects system sensitivity by viscous damping. To overcome this limitation and improve the performance of nanomotion sensors, we propose a partial-wetting nanomotion detector (PWMD) operating in a partial wetting condition. Indeed, the reduction of the liquid-sensor interface has been known to enhance the quality factor of the cantilever, by meniscus formation.[2] Our sensor consists of a silicon chip including a 500 µm large suspended window where rectangular silicon nitride cantilevers are carved in the membrane and separated from the latter by a groove (Fig. 1A). The operativity of PWMD was tested by monitoring in real time both the forces developed by breast cancer cells during adhesion process and the bacteria motility in culture media changing and upon antibiotic administration. To perform partial wetting measurements we designed and fabricated a special chamber of measurements that allowed cells to adhere on one side of the cantilever which was functionalized with 3-aminopropyltriethoxysilane, while keeping dry its backside where laser beam is reflected (Fig. 1B). The cantilever deflection was then detected by using the deflection system of a JPK Nanowizard II AFM, mounted on top of an inverted microscope.

The cantilever deflection was correlated with the motion of living cells adherent on the cantilever or on the groove as independently assessed by optical microscopy. The analysis of our data demonstrates that the PWMD system can be used to distinguish adhesion and contraction forces developed by cells (Fig.1C). Moreover, we demonstrated that our detector is capable of monitoring nanomotion of bacteria exposed to different culture media. The PWDM system represents a promising tool not only to study relevant biological processes such as cell adhesion and motility, but also to rapidly test the effect of chemotherapeutic drugs and bacterial response to antibiotics.

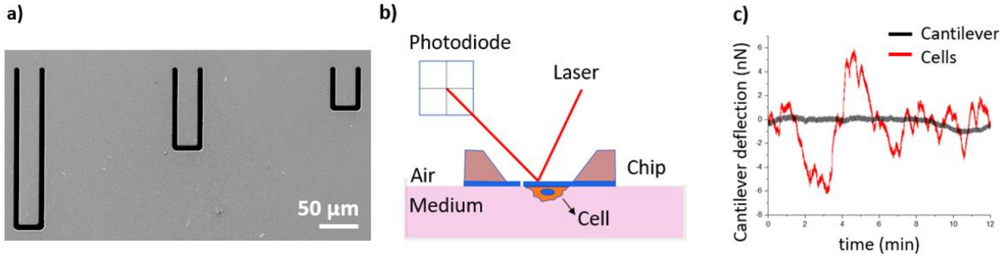

Figure 1. a) SEM image of the rectangular cantilevers separated from the membrane by a groove; b) scheme of the PWMD set-up; c) example of a the deflection curve as function of time for bare cantilever (black) and in presence of MDA-MB 231 cells (red) recorded in PW conditions.

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# Imaging and analysis at nanoscale. Merging between SPM and optics

Filippo Costa[1*] and Stefano Prato[2]

*filippo.costa@phd.units.it

[1] *Department of Physics, University of Trieste, 34100 Trieste, Italy*
[2] *A. P. E. Research srl*

The interest in the nanoparticle-based drug delivery systems (NDDSs) has grown in the past decade. This work aims to develop a protocol for the characterization of Solid Lipid Nanoparticles (SLNPs) with physical based techniques. This is done in collaboration with A.P.E. Research which designs and develops imaging and characterization instrumentations. This work is part of the project CATHENA (Cancer Therapy by Nanomedicine "POR FESR FVG PROJECT").

Now we are focusing on the identification of possible optical fingerprints from the nanoparticles. The goal is to identify if and where the SLNPs interact with carcinomic cells analyzing histological sections of tissue samples.

Through AFM, Raman spectroscopy and fluorescence spectroscopy, we performed a study on SLNPs and on Indocyanine green (ICG) dye. This study is done to understand the behavior of SLNPs and ICG once deposited on a specific substrate such as Glass, Silicon, ITO and HOPG which is not well-known as the one in solution. ICG is a fluorescent dye used in medicine as an indicator substance which is present on the nanoparticles surface. The purpose is to identify a possible characteristic that can allow a simple detection in complex systems such as tissues.

Atomic force microscopy (AFM) also integrated with kelvin probe microscopy (KPM) and electrostatic force microscopy (EFM) are also performed for the characterization of SLNPs on different substrate. Studies are done on the substrate characterization of histological samples without SLNPs, the tissue sample are excited with tree different wavelength trough different lasers and analyzed thanks to scanning near-field optical microscopy (SNOM).

The aim of this work will be the merge of those techniques. This will be used to the analysis of histological samples from subjects treated with SLNPs. Being able to detect the presence of SLNPs within tissue samples may validate possible results from the whole project.

# Design, synthesis and use of organic-inorganic nanoparticles protected by fluorinated ligands as nanomaterial for imaging and therapy

M. Cretella,* L. Pasquato and P. Pengo

*matteo.cretella@phd.units.it

*Department of Chemical and Pharmaceutical Sciences, University of Trieste, via Licio Giorgieri 1, 34127Trieste ( TS)*

Small and monodisperse gold nanoparticles (NPs) protected by self-assembled monolayer (SAM) of tailored fluorinated thiolates were synthetized as contrast agent for $^{19}F$ MRI. The thiol was designed in order to be structured as a three-blocks linear organic compound. The blocks are: a short polyethylene glycol chain for dispersibility and biocompatibility, a long linear perfluoro(polyethylene glycol) chain with a high density of (quasi)equivalent fluorine atoms for a strong and intense $^{19}F$ signal and a short mercaptoalkyl chain to link the compound to the gold core for increased system stability. Gold nanoparticles were synthetized in a single homogenous phase solution and characterized by means of TEM, NMR, UV-Vis spectroscopy, DLS and TGA. Their potential as contrast agent was determined by measuring the T1 and T2 relaxation times. The combination of the high density of fluorinated chains per NP with the small NP size (2 nm) provides a single strong signal in the $^{19}F$ NMR spectrum, leading to a promising multimodal tool for biomedical applications. Following the promising results given by the fluorinated polymer, a second amphiphilic fluorinated compound was designed for the dispersion in micelles of water-insoluble copper sulphide nanoparticles ($Cu_{(2-x)}S$) in order to broaden the scope of their application as a $^{19}F$ MRI contrast agent.

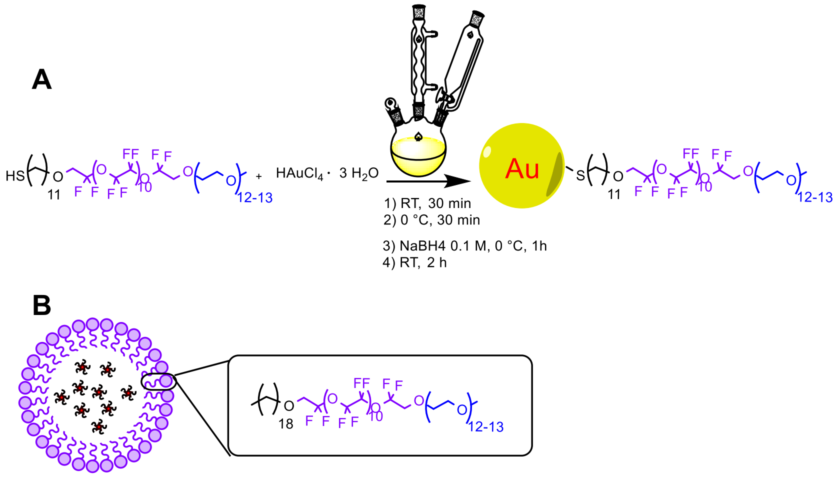

Figure 1. **A** Synthesis of gold nanoparticles (AuNPs) and **B** micellar structure of amphiphilic fluorinated compound hosting $Cu_{(2-x)}S$ NPs.

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# Light induced magnetic modifications in multiferroic heterostructures

Deepak Dagur[1,2*] Vincent Polewczyk,[2] Pietro Carrara,[2,3] Marta Brioschi,[2,3] Sara Fiori,[2] Riccardo Cucini,[2] Giorgio Rossi,[2,3] Piero Torelli[2] and Giovanni Vinai[2]

*deepak.dagur@phd.units.it

[1] *Department of Physics, University of Trieste, Via A. Valerio 2, 34127, Trieste, Italy*
[2] *Istituto Officina dei Materiali (IOM)-CNR, Area Science Park, S.S.14, km 163.5, I-34149 Trieste, Italy*
[3] *Department of Physics, University of Milan, Milano I, 20133, Milan, Italy*

The concept of designing multiferroic (MF) heterostructures to control the magnetization through the application of an electric field has driven a tremendous research effort for applications in nano-magnetism and spintronics. In particular, the possibility of setting the state of the interfacial ferromagnetic (FM) layer by switching the ferroelectric (FE) polarization of the substrate does not require application of high currents and is therefore advantageous in terms of energy dissipation and robustness. Recently photostriction[1-3] has being used as an additional parameter to influence the FM properties in MF systems since visible light excitation can induce nonthermal strain of the FE substrate, inducing modifications on the interfacial magnetostrictive layer[4-5].

In this framework, here we report results from our research on tailoring the magnetic properties on a FM/PMN-PT heterostructure by applying UV/visible light irradiation as a function of the ferroelectric polarization, for different thin FM materials and with $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3-xPbTiO_3$ ; (PMN-PT, x ranging from 25-40) as FE substrate. A photovoltaic behavior is measured during the FE polarization switching under illumination, together with the appearance of reversible surface cracks[6]. As a function of the light-induced changes in the FE substrate, Magneto-Optic Kerr Effect (MOKE) and X-ray Circular Dichroism (XMCD) measurements revealed how the modifications induced to the interfacial magnetic properties that actually depend on several parameters, such as the magnetostrictive properties of the FM layer, on the PMN-PT composition, and on the quality of the interfacial coupling.

These results show that the changes induced by illumination of the FE substrate on the magnetic behavior are maximized in the case of PMN-PT (x=40)/Ni heterostructures, where large light-induced variations on the FM coercive field are observed and maximized in case of pristine FE polarization. This work paves the way towards further research extended to other material as well as composites, to systematically investigate the effect, and identify the optimization parameters for achieving high density and low-power devices for information technology and beyond.

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# Reduced polynuclear $Pd_8$ complex for heterogeneous Suzuki-Miyaura cross-coupling reactions

Mario Daka,* Paolo Pengo, Tiziano Montini, Lucia Pasquato and Paolo Fornasiero

*mario.daka@phd.units.it

*Department of Chemical and Pharmaceutical Sciences and INSTM Trieste Research Unit, University of Trieste, 34127 Trieste, (Italy)*

Sub-nanometer transition metal clusters are emerging as very promising materials in the field of catalysis.[1] The low coordination number and precise composition of these clusters are synonyms for high activity and selectivity, respectively. The properties of metal clusters derive from their electronic structure, which is halfway to molecules and nanoparticles, thus clusters are considered the binders between homogeneous and heterogeneous catalysis.[2] Herein we report the synthesis of naked $Pd_8$ clusters by reduction ($H_2$/Ar, 300 °C, 15 h) of $Pd_8(\mu\text{-}SCH_2COOMe)_{16}$ complex,[3] previously photodeposited on $Al_2O_3$ and characterized with a range of techniques such as TEM, EDX, ICP and EXAFS. The as-prepared catalyst was tested for the Suzuki-Miyaura cross-coupling reaction displaying high activity in very short time at exceptional low Pd loading (0.2 wt%). Moreover, good tolerance toward functional group diversity was determined and recycling of the catalyst performed. All the findings pinpoint to a very active catalyst with promising broad range applications in the field of heterogeneous catalysis.

**Acknowledgements**: Interreg Strategic project Nano-Region (CUP D99F18000030002) is acknowledged for financial funding.

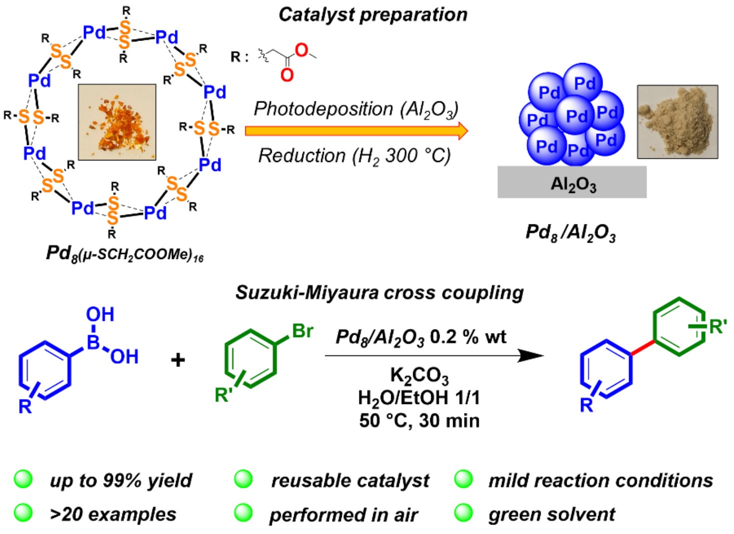

Figure 1. Catalyst synthesis (top) and $Pd_8$ catalysed cross-coupling scheme (bottom).

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# Imaging and characterization of fibrotic tissues

Lorenzo D'Amico,[1,2]* Giuliana Tromba,[2] Giovanni Birarda,[2] Lisa Vaccari,[2] Heinz Amenitsch,[3]
Loredana Casalis,[2] Lisa Vaccari[2] and Christian Dullin[3]

*lorenzo.damico@elettra.eu

[1] *Department of Engineering and Architecture, University of Trieste, via Valerio 6A, 34127 Trieste, Italy*
[2] *ELETTRA Sincrotrone Trieste S.C.p.A Basovizza, S. 14, km 163,5 in Area Science Park 34149 Basovizza (Trieste) - Italy*
[3] *Institute of Biophysics and Nanosystems Research, Austrian Academy of Sciences, Schmiedlstraße 6, 8042, Graz, Austria*
[3] *Institute of Diagnostic and Interventional Radiology, University Medical Center Goettingen, Robert Koch Strasse 40, Goettingen, Lower Saxony 37075, Germany*

Fibrosis is a general term for diseases that lead to an increased deposition of fibre, which in turn changes mechanical properties such as stiffness of an organ. This may impair the function of the organ like in the case of lung fibrosis. The lung has got a complex connective tissue comprising of several different tissue fibre types such as elastin, collagen and fibrin. During this misrouted process the pathomechanisms may involve the deposition of different fibre types. This may occur at different stages of the disease and vary in form among different subtypes of fibrosing lung disease. However, little is known about the type of fibre deposited, their orientation and the underlying pathomechanism. The idea of this project is to develop a pipeline which will involve the use of different techniques to better understand the development of lung fibrosis. Therefore, a multi approach analysis based on the following techniques: Synchrotron radiation micro-computed tomography(SR micro-CT),Fourier Transform Infrared Spectroscopy (FTIR),Small angle X-rays Scattering (SAXS),Atomic Force Microscopy (AFM) and Particle-Inducted X-Ray Emission (PIXE) is thought to characterize over 360° this pathology.
We aim to start with an animal model based on mice and then move towards human cases. This study would be of current importance since patterns of fibrosing lung injury were detected in COVID-19 pneumonia survivors.

# Nanoparticles anti-GPC1 for glioblastoma multiforme treatment

Federica Di Cintio,[1,2*] Aharon Steffè,[1,2] Nicole Crestan,[1,3] Davide Busato,[1,2] Monica Mossenta,[1,2] Idris Vruzhaj,[1,4] Monica Argenziano,[5] Roberta Cavalli,[5] Sara Capolla,[2] Paolo Macor,[2] Michele Dal Bo[2] and Giuseppe Toffoli[2]

*federica.dicintio@phd.it

[1] *Experimental and Clinical Pharmacology Unit, Centro di Riferimento Oncologico (IRCCS), Aviano, Italy*
[2] *Department of Life Sciences, University of Trieste, Trieste, Italy*
[3] *Department of Chemical and Pharmaceutical Sciences, University of Trieste, Trieste, Italy*
[4] *Department of Pharmaceutical and Pharmacological Sciences, University of Padova, Padova, Italy*
[5] *Department of Chemistry, University of Turin, Turin, Italy*

Glioblastoma multiforme (GBM) is the most aggressive diffuse glioma.[1] After standard treatment, the 2-year overall survival of GBM patients is about 25%. To overcome the big limitation in the GBM treatment, we address the challenge of developing a drug delivery system based on highly biocompatible chitosan nanobubbles (NBs)[2] conjugated with an anti-glypican1 (GPC1)[3] antibody loaded with chemotherapeutic agent. We evaluated the GPC1 as useful target for drug delivering with NBs, therefore GPC1 expression was detected *in-vitro*, in GBM cells. We assessed the localization of GPC1 protein expression on the cell surface and in the cytoplasm of GBM cell lines. In tumor sections of GBM cases, GPC1 was found overexpressed whereas in normal tissues was found not expressed. To obtain a specific anti-GPC1 antibody that recognizes the c-terminal region of GPC1 protein, we produced and characterized hybridomas for three different anti-GPC1 specific clones (A, B, C). GPC1 expression was detected in GBM cell lines at levels comparable to the levels obtained by using the commercial antibody (a-GPC1c) by the B and C clones. The A clone was not capable to recognize GPC1. Therefore, we purified the B and C clones to obtain specific anti-GPC1 monoclonal Abs. C and B appeared to be more efficient than the a-GPC1c for detection of GPC1 expression levels. According to these results the B clone was chosen to be conjugated to the NBs to develop the active drug delivery strategy. To select the drug to be loaded in the NBs, the killing capability of temozolomide (TMZ), paclitaxel (PTX) and docetaxel (DTX) was evaluated in GBM cells. DTX showed the highest killing capability. Therefore, we used DTX for the NBs loading encapsulation. The *in-vitro* characterization of NBs showed the average diameter of about 350 nm, positive charge, and spherical morphology. *In-vitro* analysis of the treatment of NBs in GBM cells showed the localization of NBs conjugated with B antibody in cell cytoplasm around the nucleus. A lower mean fluorescence was observed for the cells treated with unconjugated NBs. For the *in-vitro* cytotoxic effect of NBs, NB loaded with DTX, NBs loaded with DTX and conjugated with B antibody, showed a killing capability correlated with the concentration, with cell viable levels like those of free DTX for some concentrations. Blank NBs, NB conjugated with Cy 5.5, and NB conjugated with B antibody were not toxic at all tested concentrations. *In-vivo* and *ex-vivo* test of the biodistribution of anti-GPC1 NBs in GBM mice models, showed that the presence of the conjugation with the B antibody allows a major accumulation of the injected NBs in the tumor as well as a higher retention time at least until the last time point of treatment. In conclusion, the proposed active drug delivery approach using anti-GPC1 conjugated NBs loaded with DTX could be useful for the treatment of GBM.

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# Transfer of axial chirality to the nanoscale endows carbon nanodots with circularly polarized luminescence

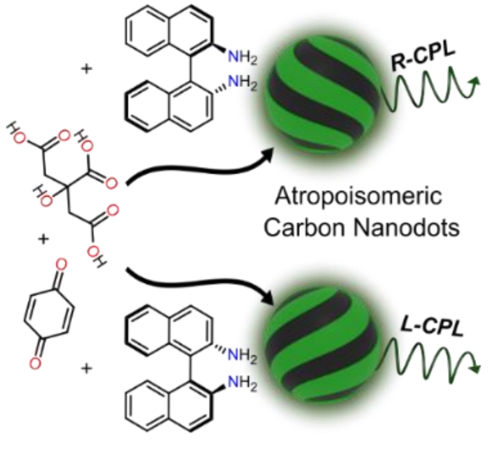
Simone Di Noja,[1] F. Amato,[1] F. Zinna,[2] G. Ragazzon,[1]* L. Di Bari[2]* and M. Prato[1,3,4]*

*ragazzon@unistra.fr, lorenzo.dibari@unipi.it, prato@units.it

[1] *Department of Chemical and Pharmaceutical Sciences, CENMAT, Center of Excellence for Nanostructured Materials, INSTM UdR, Trieste, University of Trieste, via Licio Giorgieri 1, 34127, Trieste, Italy*
[2] *Department of Chemistry and Industrial Chemistry, University of Pisa, via Moruzzi 13, 56124, Pisa, Italy*
[3] *Center for Cooperative Research in Biomaterials (CIC biomaGUNE), Basque Research and Technology Alliance (BRTA), Paseo de Miramón 182, 20014, Donostia San Sebastián, Spain*
[4] *Basque Fdn Sci, Ikerbasque, Bilbao 48013, Spain*

Carbon Nanodots (CNDs) are carbon-based nanoparticles that have recently gained great interest as novel luminescent materials.[1,2] The properties of CNDs largely depend on the type of precursors employed during the synthetic process. Our group has developed a general strategy to expand CNDs properties, by using ad hoc molecular precursors, which can transfer their features to the nanomaterial.[3]

Leveraging on our expertise in the preparation of chiral CNDs,[4] I have engineered atropoisomeric CNDs. The approach is based on a one-pot microwave-assisted solvothermal synthesis, using citric acid, 1,4-benzoquinone as dopant, and either (S)-1,1′-binaphtyl-2,2′-diamine or its (R)-atropoisomer, which impart the chirality to the nanoparticles. The obtained CNDs are soluble in common polar organic solvents, such as DMF, $CHCl_3$ and $CH_2Cl_2$, indicating good processability. After optimization of different parameters (time, temperature, amount of dopant), structural and morphological properties of CNDs were studied. As assessed by different techniques (AFM, TEM, $^1H$-NMR, FTIR, XPS, TGA), the novel CNDs show a similar dimension (medium size of 3.57 nm) and structure, regardless of the atropoisomer employed. CNDs show identical UV-Vis absorption spectra and exhibit identical fluorescence emission in the green region, with a maximum at 480 nm. Chirality of the obtained nanoparticle is confirmed by nicely specular circular dichroism spectra. Remarkably, these atropoisomeric nanoparticles show opposite CPL bands, which retrace the luminescence profile. Moreover, CNDs show high thermal stability, making them suitable for technological applications. To the best of our knowledge, this is the first example of CNDs showing intrinsic CPL emission, without the use of any external chiral matrix.[5]



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# How adsorbed H, O, OH, and Cl affect on the adsorption of imidazole on copper

Matjaž Dlouhy,[1,2]* Anton Kokalj[1,2]

*matjaz.dlouhy@ijs.si

[1] *Department of Physical and Organic Chemistry, Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia*
[2] *Jožef Stefan International Postgraduate School, Jamova 39, 1000 Ljubljana, Slovenia*

Metals exposed to real environments are never clean. Even during active dissolution in corrosion, they are likely covered with adsorbed species such as O, OH, H, and Cl (hereafter denoted $X_{(ads)}$). The first three species are typically involved in cathodic corrosion reactions, while chloride is a well-known corrosion activator. In order to investigate how the presence of these species affects the adsorption of imidazole—used as an archetypal model of azole-type corrosion inhibitors—on Cu(111), we performed a systematic high-throughput DFT study by considering more than 500 different adsorption configurations. Our calculations show that $O_{(ads)}$ and $Cl_{(ads)}$ enhance the adsorption bonding of imidazole, $H_{(ads)}$ has almost no effect, whereas $OH_{(ads)}$ either diminishes or has a negligible effect on the adsorption of imidazole. Three different co-adsorption effects of $X_{(ads)}$ on the non-dissociative adsorption of imidazole were identified. The first effect is related to the stabilization of the inhibitor molecule by the formation of a hydrogen bond between the imidazole and $O_{(ads)}$ or $OH_{(ads)}$. The second effect is due to the enhanced N–Cu bond between imidazole and the surface in the presence of $O_{(ads)}$ and $Cl_{(ads)}$. The third effect is related to a change in the work function induced by $X_{(ads)}$, which can be either stabilizing (in the case of $O_{(ads)}$ and $Cl_{(ads)}$), negligible ($H_{(ads)}$), or destabilizing ($OH_{(ads)}$) for imidazole adsorption.

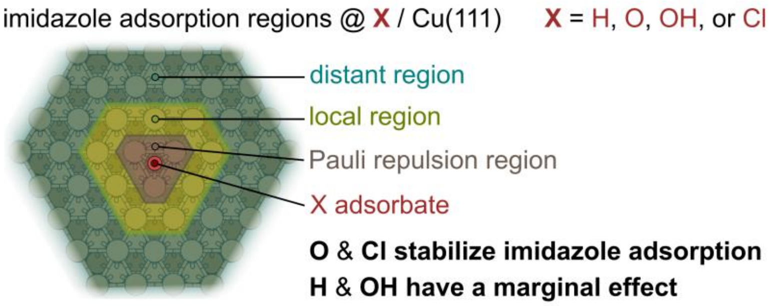

Figure 1. Three different adsorption regions of imidazole on X/Cu(111) with respect to its lateral distance to $X_{(ads)}$.

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# Reduction of matrix effect in ToF-SIMS depth profiling via $H_2$ flooding

Jernej Ekar[1,2*] and Janez Kovač[1]

*jernej.ekar@ijs.si

[1] *Jožef Stefan Institute, Jamova cesta 39, SI-1000 Ljubljana, Slovenia*
[2] *Jožef Stefan International Postgraduate School, Jamova cesta 39, SI-1000 Ljubljana, Slovenia*

The influence of the flooding gas during ToF-SIMS depth profiling was studied to reduce the matrix effect and improve the quality of the depth profiles. The profiles were measured on three multilayered samples prepared by PVD. They were composed of metal, metal oxide, and alloy layers. The thickness of the layers for different samples was between 3 and 30 nm. Dual-beam depth profiling was performed with 1 keV $Cs^+$ and 1 keV $O_2^+$ sputter beams and analysed with a $Bi^+$ primary beam. The novelty of this work was the application of $H_2$, $C_2H_2$, CO, and $O_2$ atmospheres during SIMS depth profiling. Negative cluster secondary ions, formed from sputtered metals/metal oxides and the flooding gases during $Cs^+$ sputtering, were analysed. A systematic comparison and evaluation of the ToF-SIMS depth profiles were performed regarding the matrix effect, ionization probability, chemical sensitivity, sputtering rate, and depth resolution.

We found that depth profiling in the $C_2H_2$, CO, and $O_2$ atmospheres has some advantages over UHV depth profiling, but it still lacks the information needed for an unambiguous determination of multilayered structures. However, the ToF-SIMS depth profiles were significantly improved during $H_2$ flooding in terms of matrix-effect reduction. The structures of all the samples were clearly resolved while measuring the intensity of the $M_nH_m^-$, $M_nO_m^-$, $M_nO_mH^-$, and $M_n^-$ cluster secondary ions. A further decrease in the matrix effect was obtained by normalization of the measured signals. The results were extensively presented in our recent publication (1). $H_2$ atmosphere was applied in a study of the depth profiling of thin polymer layers on the metallic substrate (2) as well as during the research of different examples of corrosion on metals and alloys (publication in preparation). Furthermore, the use of the $H_2$ shows improvement in depth resolution determined from the depth profiles as well as reduction of surface roughening during depth profiling, measured with the AFM microscope. $H_2$ flooding is, therefore, proposed for the depth profiling of metal/metal oxide multilayers and alloys, studies of corrosion as well as research of different layers deposited on the metallic substrates.

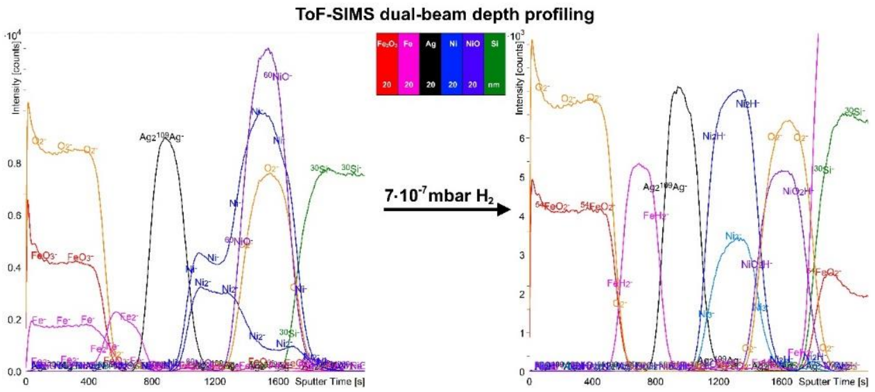

Figure 1. Comparison of the ToF-SIMS depth profiles of the sample composed of the metal and metal oxide layers measured in the UHV environment (left) and $H_2$ atmosphere (right). Depth profiling was done with the 1 keV $Cs^+$ ion beam. Pressure during $H_2$ flooding was $7 \times 10^{-7}$ mbar and $2 \times 10^{-9}$ mbar for the UHV conditions.

**Acknowledgements**: We thank Prof. Peter Panjan for the preparation of the model samples and Prof. Siegfried Hofmann for suggestions for the TiSi sample structure and composition. This work was supported by the Slovenian Research Agency (ARRS) through the Program P2-0082.

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# Label-free SERS spectroscopy: new perspectives in the bioanalytical field and biofluids analysis

Alessandro Esposito, Stefano Fornasaro, Gioia Venturotti, Alois Bonifacio and Valter Sergo

*alessandro.esposito@phd.units.it

*Department of Engineering and Architecture, University of Trieste, 34127 Trieste (Italy)*

SERS (Surface Enhanced Raman Scattering) spectroscopy is a powerful analytical technique to identify chemical species with high sensitivity. Specifically, it combines typical molecular fingerprinting of Raman vibrational spectroscopy with signal enhancement due to the presence of LSPRs (localized surface plasmon resonance), provided by specific metal nanostructured surfaces[1]. SERS has found promising applications in precision medicine and bioanalytics, such as in TDM (therapeutic drug monitoring), and clinical samples classification[2]. SERS is putatively a fast, inexpensive and user-friendly technology, competing with more complex analytical standard techniques. Specifically, in label-free SERS analytical targets directly adsorb onto the metal surface, thus requiring no metal surface functionalization. Hence, we report our recent studies to show some advancements in label-free SERS bioanalytical field. For the first-time stool samples have been characterized by SERS, highlighting the presence of specific bacterial purine metabolites. At the same extent, GCF (gingival crevicular fluid) from more than 70 teeth with and without periodontal disease have been classified on the base of SERS spectra. Interestingly SERS substrates were fabricated by centrifugation of GCF spotted paper with silver colloidal NPs (as plasmonic material)[3]. Finally, a similar approach renamed as CSPP (centrifugal silver plasmonic paper) SERS substrate has been studied and optimized in presence of rich-in-proteins biofluids, such as human serum. CSPPs has shown high signal enhancement and reproducibility of SERS spectra obtained from commercial serum.[4] Specifically, SERS serum spectra are dominated by the presence of uric acid and hypoxanthine[5], but many of them have shown the presence of very specific different bands at (485 $cm^{-1}$,1220 $cm^{-1}$,1580 $cm^{-1}$), that only recently have been attributed to the dietary amino acid ergothioneine (ET)[6]. ET seems to play an important role in regulating the oxidative stress, like other small thiol-amino acid or peptides (e.g., glutathione). This correlate with the ubiquitous expression of a specific ET transporter responsible for ET accumulation in some body districts, like blood, liver and kidney[7]. Due to the high affinity for the plasmonic metal nanostructures we reported a first attempt to quantify ET in human serum with SERS.

**Acknowledgements**: *IRCSS Materno Burlo Garofolo,* paediatric clinic, celiac diagnosis unit, Trieste and Di Lenarda's group, Department of Medical, Surgical and Health Sciences, University of Trieste.

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# Development of high-strength nanostructured multilayers for applications in nuclear fusion reactors

Ayesha Farooq,[1,2,3] Sunil Bhardwaj,[3] Simone Dal Zilio[3] and Cinzia Cepek[3]

*farooq@iom.cnr.it

[1] *Department of Physics, University of Trieste, Italy*
[2] *COMSATS University Islamabad, Pakistan*
[3] *Istituto Officina dei Materiali – CNR, Laboratorio TASC Area Science Park - Basovizza, Edificio MM Strada Statale 14, Km.163.5 I-34149 Trieste, Italy*

Achieving clean, safe and revolutionary energy can be found in the stars and in their nuclear fusion, as it would be able to produce large quantities of energy safely, virtually inexhaustible and without any emission of greenhouse gases. Despite all the efforts, the road to nuclear fusion still seems very long, and many aspects in the realization of a fusion reactor needs to be solved. The first wall materials of a Nuclear Fusion reactor face the most extreme conditions, like high heat loads, thermal shocks, bombardment of neutrons and tritium retention and still it is needed to find innovative solutions, exploring the limits of material science. This PhD project aims at the synthesis and study of carbon and tungsten hybrid nano-materials of controlled and reproducible size and morphology for applications in fusion reactors[1]. Graphite and tungsten have currently been identified as being among the best materials for use in nuclear fusion reactors, and their combinations in hybrid materials can change and enhance the properties of both[2,3]. Here, different carbon nanostructures (C-NSs) were grown on Silicon wafer via chemical vapour deposition (CVD) using Fe and Ni as catalyst. The obtained C-NSs will be incorporated inside tungsten films deposited via DC magnetron sputtering. We have spanned a variety of CVD and magnetron sputtering parameters, like pressure, precursor gasses and catalyst, substrate temperature, etc. All films have been analyzed by using different experimental techniques, including X-ray photoemission spectroscopy (XPS) and scanning electron microscopy (SEM), allowing to understand how the different process parameters influence the final properties of the synthetized films like, for example, their morphology, stoichiometry and electronic properties.

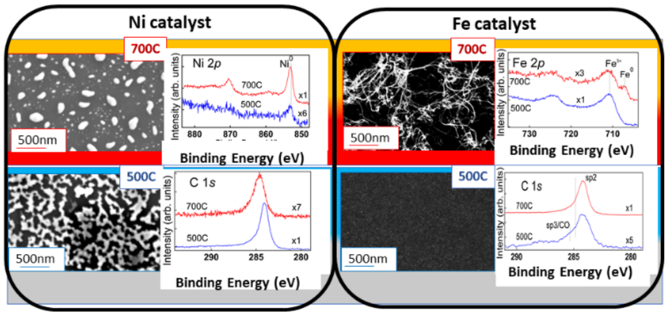

Figure 1: SEM images and relative XPS spectra of C-NSs synthetized using different catalysts (Ni, Fe) and CVD temperatures (500C, 700C). The used CVD precursor gasses were $C_2H_2$ (100sccm) and $H_2$ (100sccm) and the processes duration was 5-10 min.

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# Effects of $SO_2$ trace impurities in $CO_2$ feed on copper and Tin based catalysts during $CO_2RR$

Marcello Ferrara,[1] Subhajyoti Samanta,[2] Manuela Bevilacqua,[3] Michele Melchionna,[1] Jonas Baltrusaitis[2] and Paolo Fornasiero[1,3]*

*pfornasiero@units.it

*[1] Department of Chemical and Pharmaceutical Sciences, INSTM. University of Trieste, Trieste, Italy*
*[2] Department of Chemical and Biomolecular Engineering, Lehigh University, Bethlehem (PA), USA*
*[3] ICCOM-CNR – Trieste Research Unit, Trieste, Italy*

The $CO_2$ electrochemical reduction reaction ($CO_2$eRR) has been a topic of research for decades[1], promising a way to reuse our omnipresent waste gas $CO_2$. In particular, $CO_2$eRR can run in water-based electrolyzers (thus at room temperature and pressures), resulting in a green process that could give new value to a waste gas. However, few studies have been performed to understand the influence of gaseous impurities in $CO_2$ electroreduction[2,3]. This is particularly important if $CO_2$ is collected from industrial settings, where many sulfur and nitrogen compounds have a significant concentration and could have an impact on catalytic activity. Various copper/tin oxide materials were synthesized with different Cu:Sn ratios. The presence of $SO_2$ in the $CO_2$ gas feed reduces the faradaic efficiency for all $CO_2$RR products and can be reduced by the catalyst itself to sulfur-based gases or poisoning the surface with sulfur adducts. Preliminar tests on copper electrodes show drastic changes in the $CO_2$RR selectivities but otherwise stable activity with 1% $SO_2$ impurity. Other research is needed on the tin-based materials, given the higher resistance that these materials have shown in literature.[2]

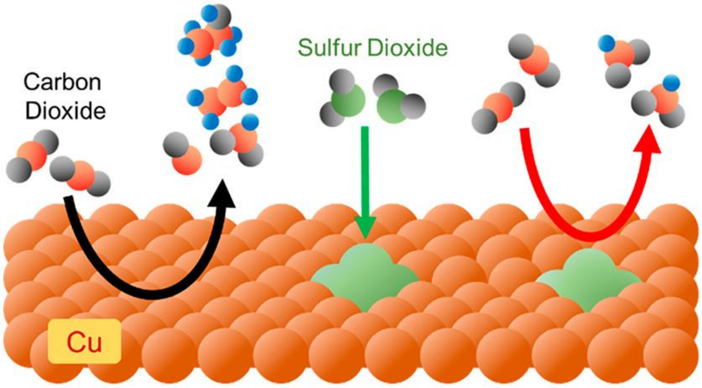

Figure 1. $CO_2$ reduction on copper can be affected by the reaction of the surface with sulfur dioxide to change its selectivity. Reprinted with permission from reference 2. Copyright 2021 American Chemical Society.

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# Immunocompatibility and biomedical applications of new nanomaterials

Arianna Gazzi,[1,2] , Laura Fusco,[2,3] Linda Giro,[2] Maurizio Prato[1] and Lucia Gemma Delogu[2*]

*luciagemma.delogu@unipd.it

[1]*Department of Chemical and Pharmaceutical Sciences University of Trieste, Trieste, Italy*
[2]*Department of Biomedical Sciences, University of Padua, Padua, Italy*
[3]*A. J. Drexel Nanomaterials Institute and Department of Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania, USA*

Nanomaterial's properties can be exploited for diagnostics, therapy, or theranostics[1,2]. Following exposure, particularly intravenous injection, these nanomaterials can be recognized by immune cells as the body's first defensive barrier. This interaction could be modulated by the different physicochemical properties of the materials (i.e., structure, size, and surface chemistry) by either stimulating or suppressing the immune response. Therefore, a critical step for future translational applications is represented by the assessment of nanomaterial's impact on the immune system.

In this view, the nanoimmunity-by-design concept[3] is a harmonized cutting-edge approach for the nanomaterials characterization based not only on a chemical-physical point of view but also on the effects on the immune system. In this work, human primary immune cell populations were chosen to develop a new experimental model that can be adopted for the immune assessment of a large number of nanomaterials. As a proof of concept, the project focused on the immunological characterization of some of the most disparate promising nanomaterials for biomedical applications: carbon nanodots, ultrasmall silica nanoparticles, graphene-oxide-based hydrogels, titanium-based transition metal carbides, and polystyrene nanoparticles, adopting single-cell level techniques (i.e., flow cytometry and single-cell mass cytometry).

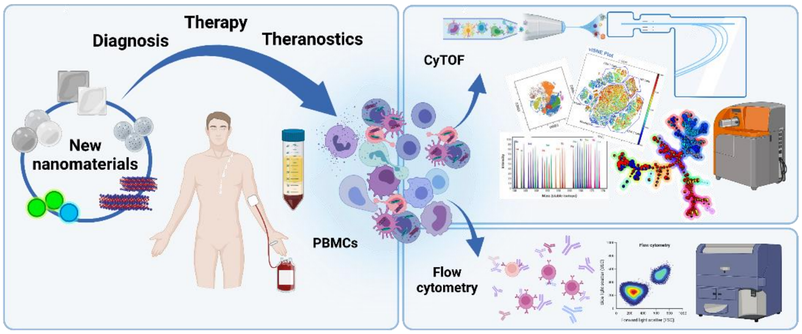

Figure 1. Workflow of the study showing the immunological characterization of new nanomaterials for biomedical applications.

**Acknowledgements**: The authors thank the MIUR JTC Graphene 2015 (G-IMMUNOMICS project) and the European Union's HORIZON 2020 research and innovation program under MSCA RISE 2016 project Carbo-IMmap grant. n. 734381.

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# Direct foaming of CRT waste glass in air atmosphere

Uroš Hribar[1,2], Matjaž Spreitzer[1] and Jakob König[1]

*uros.hribar@ijs.si

[1] *Advanced Materials Department, Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia*
[2] *Jožef Stefan International Postgraduate School, Jamova cesta 39, 1000 Ljubljana, Slovenia*

A combination of useful properties along with longevity and the ability to be produced from waste glass are the main reasons why foamed glass is considered a "green" construction insulation material. However, commercial production of high-quality waste-based foamed glass still requires relatively large energy input. This aspect could be improved by avoiding the glass melting step and/or control over the furnace atmosphere. In this research, we prepared foamed glass based on waste cathode ray tube (CRT) television panel glass via direct foaming without the melting step and without a special furnace atmosphere, i.e. heat treatment was done in the air. We propose a foaming mechanism based on the behavior of the material during heating, by measuring the pre- and post-reaction densities of the samples, hot-stage microscopy, thermal analysis (TA) coupled with a mass spectrometer (MS), X-ray diffractometry (XRD), infra-red spectroscopy (IR) and gas chromatography (GC).

The addition of water glass to the foaming mixture of milled CRT panel glass, carbon black, $Mn_3O_4$ and $K_3PO_4$ suppresses the oxidation of carbon black at lower temperatures (< 600 °C) which enables the implementation of the foaming process in the air atmosphere. Two major contributions to the expansion of the material were determined; i) reaction between carbon and $Mn_3O_4$ and ii) direct contribution from water glass. Results of GC and IR suggest that direct contribution to the expansion from water glass happens due to the formation of carbonates during the preparation stage and their subsequent decomposition. Most promising foamed glass samples prepared via investigated procedure had an apparent density of 0.145 g $cm^{-3}$ with corresponding thermal conductivity of 0.039 W $m^{-1}$ $K^{-1}$. In the second part of the research, we demonstrate that process can be implemented in the air atmosphere without the addition of water glass, by using hydrothermally treated CRT glass powder.

With this research, we demonstrate the implementation of the foaming process based on the carbonaceous foaming agent in the air atmosphere with the use of hydrated silicates. Additionally, we propose a new mechanism of foaming with water glass via carbonate formation. Foamed glass samples from this research have comparable properties to some of the best commercial products despite being prepared with a less energy-intensive process based on waste glass. Avoiding energetically expensive parts of the process, without significantly hindering the properties of the material, could make the process interesting for further research and have an impact on future trends in the foamed glass community.

# Optimization of semiconductor-superconductor nano-systems for the development of Andreev qubits

M. Kirti,[1,2*] A. Benali,[2] S. Csonka,[3] M. Sütő,[3] E. Tóvári,[3] P. Makk,[3] P. L. Neumann and G. Biasiol[2]

*magdhi.kirti@phd.units.it

*[1] Department of Physics, University of Trieste, Piazzale Europa 1, 34127 Trieste, Italy*
*[2] OM CNR, Laboratorio TASC, Area Science Park Basovizza, 34149Trieste, Italy*
*[3] Department of Physics, Budapest University of Technology and Economics, 1111 Budapest, Hungary*

Two-dimensional electron systems confined to the surface of narrowband semiconductors have piqued interest due to their ease of integration with superconductivity, allowing for new hybrid device systems. These hybrid systems lay the foundations of a radically new solid-state platform for scalable quantum computing based on Andreev quantum bits (qubits). These Semiconductor-superconductor hybrid systems resulting in Andreev qubits are among the promising candidates, as high-quality superconducting thin films with transparent interfaces to a low-D semiconductor will make it possible to improve the coherence time and strong qubit-qubit coupling.[1,2] The InAs 2D electron gases (2DEGs) are the ideal semiconductor systems due to their vanishing Schottky barrier; however, their exploitation is limited by the non-availability of commercial lattice-matched substrates.[3,4]

In this work we have demonstrated that in-situ growth of Aluminum films on near-surface InAs 2D electron gases (2DEGs) can be grown by Molecular Beam Epitaxy on GaAs substrates with quality comparable to state-of-the art growth on InP despite 7% InAs/GaAs lattice mismatch.[5] Adaptation of the metamorphic growth protocol has allowed to reach low-Temperature electron mobilities up to $8X10^5 cm^2/Vs$ in undoped deep $InAs/In_{0.81}Ga_{0.19}As$ 2DEGs, while preserving values around $5X10^4 cm^2/Vs$ for 2DEGs at 10nm from the surface, with a charge around $3.5X10^{11}/cm^2$.

In-situ growth of Al films resulted in crystalline thin films with the coexistence of different crystallographic domains. Atomic force microscopy (AFM) and X ray reflectivity (XRR) showed that Al deposition is conformal to that of the underlying semiconductors, which preserved the cross-hatched pattern typical for metamorphic growth. Resistivity as a function of temperature was comparable to the best Al layers on GaAs and superconducting proximity effect was observed in a Josephson junction. The growth protocol developed could thus set a new standard for the fabrication of Andreev qubits on GaAs technology.

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# Preparation of BN graphene quantum dots and investigation of their photophysical and electrochromic properties

Veronika Kost* and Tatiana Da Ros

*veronika.kost@phd.units.it

*Department of Chemical and Pharmaceutical Sciences, University of Trieste, Piazzale Europa 1, 34127, Trieste, Italy*

Graphene quantum dots (GQDs) are a promising class of carbon nanomaterials characterized by unique photophysical and photochemical properties, which can be adjusted by using adapt preparation methods.[1] Despite the wide range of synthesis routes suitable for GQDs production, achieving reproducible and properly controllable synthesis remains a challenging task.[2,3]

In this study, the synthesis of B, N-doped graphene quantum dots was carried out by bottom-up techniques starting from different precursors, including melamine and its polymer, or a mixture of citric acid, boric acid, and urea. The preliminary characterization of the obtained nanomaterials was carried out by spectroscopic (DLS, FT-IR, FL, UV-vis) and microscopic (TEM) analyses. The synthesis conditions, as well as ratios of the reagents, were varying to get control over the structure, size, and composition and, as a consequence, their photophysical properties. By microwave treatment of a mixture of citric acid, boric acid, and urea, we obtained B, N-doped carbon dots with the uniform average size of 4 nm (Fig.1 a), presenting quantum yield of 34%, and excitation independent photoluminescence behavior in the blue region (Fig.1 b). The obtained nanomaterials, after further characterization by HR-TEM, AFM, and XPS analyses, will be tested for possible applications in optoelectronic devices.

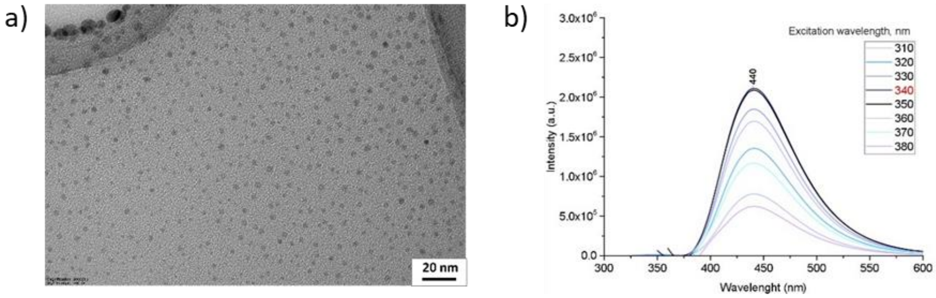

Figure 1. TEM image (a) and FL spectra (b) of B, N-doped GQDs obtained from citric acid, boric acid, and urea under microwave irradiation.

**Acknowledgements**: This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 956923 – STiBNite.

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# Charge dynamics in complex 2D heterostructures

Claudio Lentini Campallegio

s251546@ds.units.it

*Department of Physics, University of Trieste, Via A. Valerio 2, 34127, Trieste, Italy*

I synthesized a 2D Covalent Organic Framework (2D-COF) made of boroxine rings on top of Au (111) surface, by deposition in ultra-high vacuum conditions (UHV) and then thermal annealing of bis pinacolato di-boron (BPDB). We then characterized the resulting network by means of XPS, UVPES, ARPES and NEXAFS spectroscopy, to evaluate the structure and the electronic properties.

Boronic acids are known to be able to create 2D networks constituted of rings made of alternating B and O atoms, called boroxine rings, both in aqueous solution and in UHV conditions, that present interesting electronic and morphological properties.

A recent report showed that a boroxine network synthesized starting from tetrahydroxydiboron (THDB), presented remarkable charge transport properties towards the Au (111) surface,[1] with the creation of preferential channels for electronic transport between the metal and the COF. Following these findings, I used a similar synthesis protocol, depositing Bis Pinacolato Di-Boron (BPDB), the Pinacole ester of THDB, on top of the gold surface and then treating it thermically to create the boroxine structure. This molecule was chosen because it undergoes thermal de-esterification in UHV conditions,[2] and this behavior could allow for a fine tuning of the boroxination process using controlled deprotection. The material was then analyzed by means of XPS, ARPES and NEXAFS spectroscopy.

The XPS results showed a shift of the B1 peak after the thermal treatment and a decrease of the O/B ratio from around 2:1 to 1:1, compatible with the formation of the boroxine network, as found for the THDB. Also, the C1s signal of the pinacole chain decreases after the annealing, disappearing after treatment at 150 °C indicating that a de-esterification occurs on the sample, that is completed at around that temperature.

The ARPES study showed that after the annealing the material present band dispersion, and that the band shape and position are similar to the boroxine network formed by the THDB.

The B1s NEXAFS showed that the thermal annealing causes the disappearance of a low binding energy peak and the appearance of a peak at higher binding energy, attributable to a B atom that has a strong interaction with the surface. We reasoned that this interaction between the B and the Au(111) surface could in some way weaken the B-C bond, and therefore ease the thermal de-esterification of the pinacole molecule.

These results show that protected boronic acid are a promising raw material for producing covalent frameworks with interesting electronic and morphological properties.

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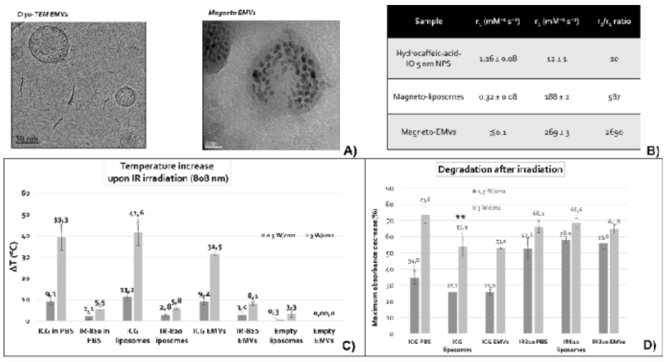
# Erythrocyte-derived carriers for theranostics applications

Giulia Della Pelle[1,2]* and Nina Kostevsek[1]
* giulia.della.pelle@ijs.si

[1] *Nanostructured materials, Jožef Stefan Institute, Ljubljana, Slovenia*
[2] *Mednarodna šola Jožefa Stefana, Ljubljana, Slovenia*

The so-called "nanorevolution", begun in the second half of the twentieth century, kept raging in drug delivery development. Over sixty nanodrug formulations have been approved worldwide so far [1], while the number of published paper is steadily increasing every year [2]. At the same time, erythrocytes, natural carriers of oxygen and carbon dioxide and able to reach nearly every district of the body, were started to be considered as the perfect match between safety and cost [3]. Erythrocytes' cell membrane is, indeed, an excellent starting material for liposomal-like formulation: they possess on their surface CD47, a "don't eat me!" marker for macrophages, escaping therefore immune system recognition. Erythrocyte-membrane vesicles (EMVs) can be produced via shear stress processes over hemoglobin-depleted erythrocytes, consisting of merely double layer, integral proteins, and cytoskeleton. We chose this model to develop a theranostic platform (i.e. a *portmanteau* for therapy + diagnostics), loading EMVs with MRI $T_2$ contrast agent and cyanine dyes for IR *in vivo* imaging. In the first case [4], we demonstrated how EMVs loaded with oleylamine-coated 5 nm iron oxide nanoparticles show superior properties compared to an approved thermolabile liposomal formulation, conferring them higher $r_2$ relaxivity times. In the second case[5], we successfully loaded indocyanine green, a worldwide approved cyanine dye, and IR-820, similar but more water-soluble, into EMVs and proved their superiority as a carrier. Both dyes, when encapsulated, indeed, not only retained their photothermal effect upon far-red laser irradiation, but in the case of indocyanine green also its degradation was significantly reduced, therefore minimizing the production of potentially harmful decomposition products. We are currently working on a dual system containing both agents.



| Sample | $r_1$ ($mM^{-1} s^{-1}$) | $r_2$ ($mM^{-1} s^{-1}$) | $r_2/r_1$ ratio |
|---|---|---|---|
| Hydrocaffeic-acid-IO 5 nm NPS | 1.16 ± 0.08 | 12 ± 1 | 10 |
| Magneto-liposomes | 0.32 ± 0.08 | 188 ± 2 | 587 |
| Magneto-EMVs | ≤0.1 | 269 ± 3 | 2690 |

Figure 1. A) Left picture, cryo-TEM micrography of empty EMVs; right picture, magneto-EMVs cryo-TEM micrography. B) Summary table of properties of carriers and coatings tested in (4). C) Photothermal effect, in terms of temperature (°C) increase upon IR irradiation5. D) Photodegradation of free and encapsulated dyes5.

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# Characterization of the localized corrosion phenomena of Al/Cu galvanic couple by scanning electrochemical microscopy

Dževad K. Kozlica,[1,2] Javier Izquierdo,[3,4] Ricardo M. Souto, [3,4,*] and Ingrid Milošev[1*]

*rsouto@ull.es (R.M. Souto) and milosev@ijs.si (I. Milošev)

[1] *Jožef Stefan Institute, Department of Physical and Organic Chemistry, SI-1000 Ljubljana, Slovenia*
[2] *Jožef Stefan International Postgraduate School, SI-1000 Ljubljana, Slovenia*
[3] *Department of Chemistry, Universidad de La Laguna, P.O. Box 456, La Laguna, Tenerife E-38200, Spain*
[4] *Institute of Materials and Nanotechnology, Universidad de La Laguna, P.O. Box 456, La Laguna, Tenerife E-38200, Spain*

Scanning electrochemical microscopy (SECM) is a microelectrode technique that is considered very attractive because it combines high spatial and electrochemical resolution giving localized *in situ* information about the processes involved in corrosion reactions[1,2]. Two corrosion inhibitors were tested on an Al/Cu model that simulates the intermetallic phase in a 2024-T3 aluminium alloy widely used in the aerospace and automotive industries[3,4]. Localized corrosion phenomena and inhibition effects in aggressive chloride environments have been observed in various SECM regimes that allow monitoring of hydrogen detection, oxygen consumption, and determination of conductive or insulating characteristics of the substrate surface[1,2].

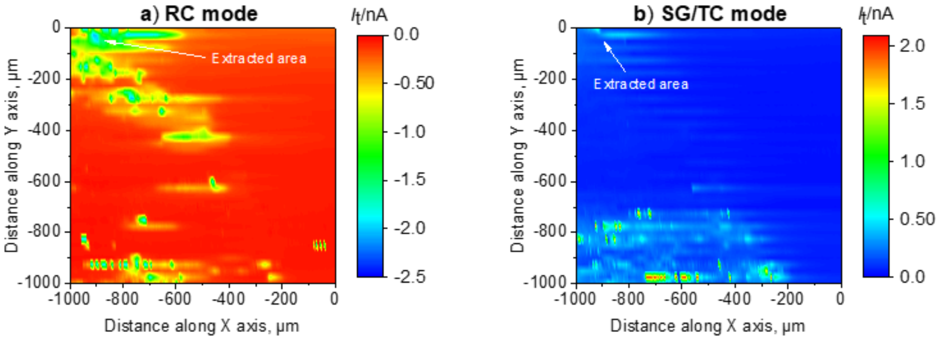

Figure 1. Images of physically and electrically coupled Al/Cu sample generated by SECM in a) redox competition mode (consumption of oxygen) after 1 min of immersion and b) substrate generation-tip collection mode (hydrogen detection) after 33 min of immersion in 50 mM NaCl solution at open circuit potential.

**Acknowledgements**: D.K. K expresses his gratitude to Ad Futura for providing the PhD scholarship through the Public scholarship, development, and maintenance fund of the Republic of Slovenia (grant no. 11011-116/2017-13) and Erasmus+ scholarship for a three-month research stay at the Universidad de la Laguna (Spain).

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# The smallest silver oxide

Federico Loi,[1] Monica Pozzo,[2] Luca Sbuelz,[1] Luca Bignardi,[1] Paolo Lacovic,[3] Ezequiel Tosi,[3] Silvano Lizzit,[3] Aras Kartouzian,[4] Ueli Heiz,[4] Dario Alfè[2,5] and Alessandro Baraldi[1,3*]

*alessandro.baraldi@elettra.eu

[1] *Department of Physics, University of Trieste, via Valerio 2, 34127 Trieste, Italy*
[2] *Department of Earth Sciences and London Centre for Nanotechnology, University College London, Gower Street, London WC1E 6BT, UK*
[3] *Elettra Sincrotrone Trieste, AREA Science Park, 34149 Trieste, Italy*
[4] *Department of Chemistry, Technical University of Munich, Lichtenbergstrasse 4, 85748 Garching, Germany*
[5] *Department of Physics Ettore Pancini, University of Napoli Federico II, Monte S. Angelo, I-80126 Napoli, Italy.*

Atomic clusters are an ensemble of few atoms and represent a bridging link between single atoms and nanoparticles. Their dimensions stay limited in the sub-nanometric range, where the structural properties are no longer dominated by the atomic structure of the outer crystal plane, as it is in the case of nanoparticles, but depend on the exact number of atoms composing the clusters.[1,2] For these systems, there is still open debate on the structure behavior in elementary processes such as oxidation, and in particular whether the local geometric configurations and oxidation states are similar or consistently altered in the sub-nanometric range with respect to bulk oxides. To address this issue and gain insight into its atomistic behavior, we studied the oxidation of an $Ag_{11}$ cluster. The oxidation was achieved inducing the dissociation of $O_2$ molecules phyisorbed on the cluster with soft X-rays, with a temperature T = 20 K and an $O_2$ background pressure of $10^{-9}$ mbar. We found that the $Ag_{11}$ cluster begins deforming as its oxygen coverage increases to present finally a local $AgO_4$ configuration and a spatial charge distribution very similar to that of silver bulk oxides. This result highlights, unlike to what happens for metal clusters, how bulk oxide conformations can start to develop already for extremely small atomic aggregates (< 1nm). This local configuration shows the lowest oxygen vacancy formation energy in the system, hence hinting at the possibility of incorporating clusters of much smaller size than nanoparticles in important catalytic reactions.

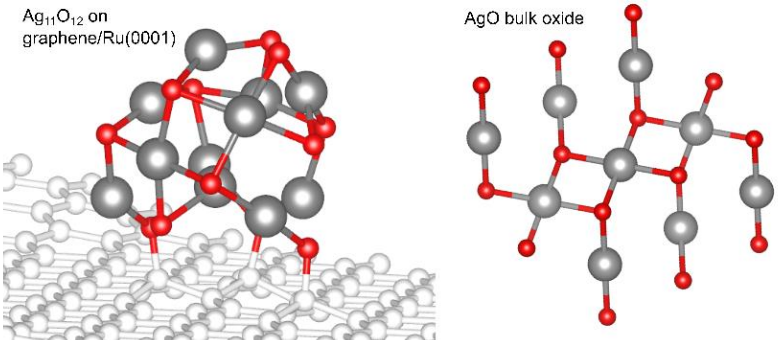

Figure 1. Structural comparison between $Ag_{11}O_{12}$ cluster (left) and AgO bulk oxide (right). The hybrid structure composed of Ag(I) and Ag(III) ions bounded to two and four O atoms and the related local $AgO_4$ configuration of AgO is preserved in the cluster.

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# Investigation of the surface reactivity of catalysts by operando X-ray absorption spectroscopy with synchrotron radiation

S. Mauri,[1,2]* D. W. Boukhvalov,[3,4] L. Braglia,[1] G. D'Olimpio,[5] A. Politano[5,6] and P. Torelli[1]

* mauri@iom.cnr.it

*[1] CNR - Istituto Officina dei Materiali, TASC, I-34149 Trieste, Italy*
*[2] Department of Physics, University of Trieste, Via Valerio 2, 34127 Trieste, Italy*
*[3] College of Science, Institute of Materials Physics and Chemistry, Nanjing Forestry University, Nanjing 210037, P. R. China*
*[4] Institute of Physics and Technology, Ural Federal University, Mira Street 19, 620002 Ekaterinburg, Russia*
*[5] INSTM and Department of Physical and Chemical Sciences, University of L'Aquila, via Vetoio, 67100 L'Aquila (AQ), Italy*
*[6] CNR-IMM Istituto per la Microelettronica e Microsistemi, V CNR-IMM Istituto per la Microelettronica e Microsistemi, VIII strada 5, I-95121 Catania, Italy III strada 5, I-95121 Catania, Italy*

The use of the innovative reaction cell for the *operando* AP-NEXAFS spectroscopy, developed at the APE-HE beamline at Elettra Synchrotron [1], allowed an investigation of the catalytic properties of pre-oxidized and pre-reduced Ni-Sn compounds with different Sn content ($Ni_3Sn_2$ and $Ni_3Sn_4$). The reaction investigated was the $CH_3OH$ decomposition to syngas ($H_2$ + CO).[2] Exploiting a multi-technique approach, i.e. combining *operando* NEXAFS with DFT calculations and *in situ* XPS characterization, this study allowed to correlate the catalytic activity of the compounds with the electronic structure modifications occurring at the sample surface, thus giving important information about the reaction mechanism. The results show that a higher surface Sn content improves the selectivity towards $H_2$ and CO. This effect is more evident when the samples are pre-oxidized. Indeed, the Sn oxide external skin partially protect the Ni atoms from irreversible chemical modifications, especially at lower temperatures (250°C). At the same time, Sn atoms are able to suppress the secondary reactions without deactivating the catalyst. This study opens new perspectives for the use of these low-cost Sn rich catalysts at low temperatures.

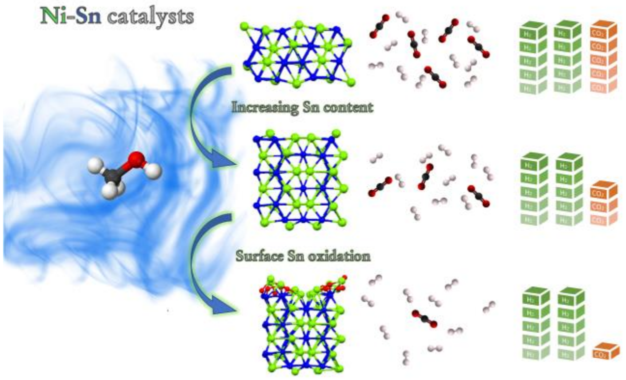

Figure 1. Graphical abstract of the work presented, showing how the selectivity to $H_2$ increases with the Sn content and with the catalyst surface oxidation.

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# Set-up of anti-GPC3-driven polymeric nanoparticles in hepatocellular carcinoma

Monica Mossenta,[1,2*] Davide Busato,[1,2] Sara Capolla,[1,2] Monica Argenziano,[3] Federica Di Cintio,[1,2] Aharon Steffé,[1,2] Roberta Cavalli,[3] Paolo Macor,[1] Michele Dal Bo[2] and Giuseppe Toffoli[2]

*monica.mossenta@phd.units.it

[1] *Department of Life Sciences, University of Trieste, 34127 Trieste, Italy*
[2] *Experimental and Clinical Pharmacology Unit, Centro di Riferimento Oncologico di Aviano (CRO), IRCCS*
[3] *Department of Drug Science and Technology, University of Turin, 10125 Turin, Italy*

Hepatocellular carcinoma (HCC) is the third leading cause of cancer-related death due to a delayed diagnosis and therapies' side-effects.[1] Based on these needs, my PhD project evaluated the use of polymeric nanoparticles made of chitosan (CS-NPs) or of poly lactic-co-glycolic acid and polyvinyl alcohol (PLGA-PVA-NPs) as candidates for a delivery strategy. Further, the anti-glypican 3 antibody 4A1, was evaluated as targeting agent, on the nanoparticles surface, in in-vivo approaches since glypican 3 is a characteristic cell surface protein of HCC.[2] Empty CS-NPs and PLGA-PVA-NPs showed no *in-vitro* cytotoxicity on HUH-7 cells (HCC cell line). The coating with 4A1 antibody (CS-4A1-NPs and PLGA-PVA-4A1-NPs) did not change nanoparticles cytotoxic behavior. In-vivo analysis were performed in athymic nude mice presenting a subcutaneous HUH-7 tumor. For these studies, CS-NPs and CS-4A1-NPs, were labelled with cyanine 5.5 and intravenously injected into the tail vein. Comparing CS-NPs and CS-4A1-NPs biodistribution at the tumor site, the presence of 4A1 increased the accumulation of the nanoparticles at 48 hrs post injection (Figure 1).

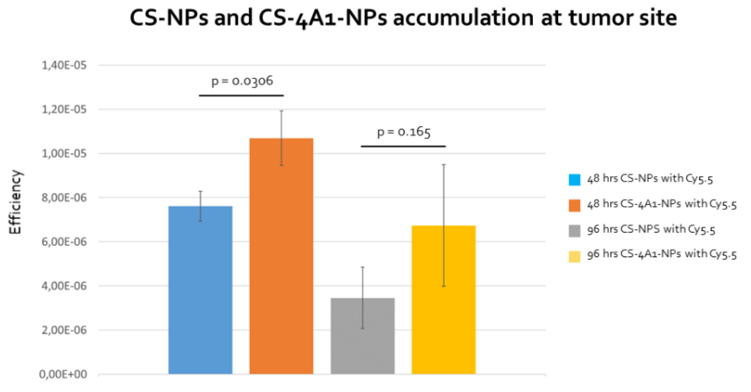

Figure 1. Ex-vivo accumulation of CS-NPs and CS-4A1-NPs at HUH-7 tumor mass. Ex-vivo analysis of the HUH-7 tumor showed a higher accumulation of CS-4A1-NPs with respect to CS-NPs, at 48 hrs post-injection. No significant differences at 96 hrs. Data: means ± S.D.

**Acknowledgements**: I would like to thank the nanomedicine group, my supervisor Dr. Giuseppe Toffoli, and our collaborators.

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# Biophysical analysis of small extracellular vesicles (sEVs) and their interaction with model plasma membrane

C. Paba,[1.] V. Dorigo,[2] B. Senigagliesi,[3] H. Vondracek,[4] V. Rondelli,[5] P.Parisse[6] and L.Casalis[4*]

*[1] University of Trieste, Trieste, Italy; [2]Hochschule Fresenius, Idstein, Germany; [3] SISSA, Trieste, Italy; [4]Elettra Sincrotrone Trieste, Trieste, Italy; [5] University of Milan, Milan ,Italy; [6]IOM-CNR, Trieste, Italy;*

**loredana.casalis@elettra.eu*

Small extracellular vesicles (sEVs) are nanometer-sized vesicles (30-200 nm) that are released from the vast majority of cells both in pathological or physiological conditions. These biological nanoparticles have shown potential for cancer diagnostics/therapeutics as they travel in bodily fluids (blood, saliva) to carry biological information between distant cells. However, because of their high heterogeneity (e.g. origin, composition, size), the processes of EV biogenesis, release and uptake are still subject of debate, as well as the involved targeting cell receptors and internalization pathways (e.g. cell membrane fusion and endocytosis).

Here we propose an assay based on Atomic Force Microscopy, to reveal purified EVs' structure-function correlations, obtained from two breast cancer cell lines with different aggressiveness. Their interaction with lipid model membrane systems with variable composition (e.g. mixing of glycolipids, sphingolipids, cholesterol) and in different environmental conditions (e.g. temperature, pH, buffer) has been tested; functional molecules such as tetraspanin proteins have been added to clarify their role in EV uptake. Preliminary AFM analysis, performed with sEVs isolated from human umbilical cord-derived mesenchymal stromal cells (UC-MSCs) as a reference sample, revealed different interaction mechanisms of EVs with lipid model membranes depending on the adopted isolation method, salt concentration, and cholesterol percentage. In both cases, a preferential interaction with raft-like lipid domains has been observed. These results lead to a better understanding of both the EVs uptake mechanisms by recipients cells and the relevant parameters involved in the EVs' selective targeting in tumor microenvironments.

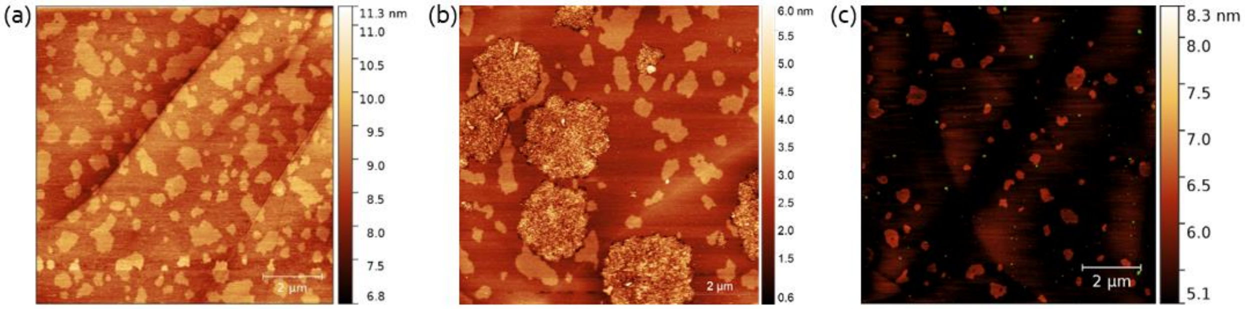

Figure 1. AFM topographic images of a DOPC : SM : Chol (2 : 1 : 0.17) SLB before (a) and after the addition of sEVs from UC-MSC cell line (b). We also report the SLB enriched with CD63 protein (c).

**Acknowledgements**: We thank M. Gimona (*Paracelsus Medical University, Salzburg, Austria)* for providing the samples. We also acknowledge L. Vaccari (Beamline SISSI Bio, Elettra Sincrotrone Trieste) for the use of their facilities. This work was supported by CERIC-ERIC.

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# Subgap states in superconducting islands

Luka Pavešič[1,2*] and Rok Žitko[1,2]

*luka.pavesic@ijs.si

[1] *Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia*
[2] *Faculty of Mathematics and Physics, University of Ljubljana, Jadranska 19, SI-1000 Ljubljana, Slovenia*

The local magnetic moment of an interacting quantum dot can be screened by a Bogoliubov quasiparticle from a nearby superconductor. This gives rise to a long lived discrete spin singlet state inside the superconducting gap, known as the Yu-Shiba-Rusinov (YSR) state. Its energy can be controlled by gate voltages in experiment, allowing for various quantum technology applications.

We study the nature of the subgap states in a quantum dot coupled to one or two superconducting islands. These are described by a model which incorporates the charging energy of the superconducting islands, important for small islands. For charging energy comparable to the superconducting gap, the subgap states are stabilized by a combination of Kondo exchange screening and charge redistribution driven by the Coulomb interaction. The model predictions match experimental results very well.

There are two singlet subgap states in the case of a quantum dot embedded between two superconducting channels, corresponding to the formation of a YSR singlet in each channel. The system can be tuned to a regime where the subgap states can be put into a superposition and coherently manipulated by electronic pulses. Such a qubit could be implemented using known technology.

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# Methods of catalyst preparation for ammonia decomposition

Žiga Ponikvar,[1*] Janvit Teržan,[2] Blaž Likozar,[3] and Sašo Gyergyek[4]

*ziga.ponikvar@ijs.si

[1] *Jožef Stefan Institute, Jamova cesta 39, Slovenia*
[2] *National Institute of Chemistry, Hajdrihova ulica 19, Slovenia*
[3] *National Institute of Chemistry, Hajdrihova ulica 19, Slovenia*
[4] *Jožef Stefan Institute, Jamova cesta 39, Slovenia*

Various preparation procedures of Ru-based catalysts will be discussed. Furthermore, a set of experiments was performed in order to evaluate different methods of metal deposition. The model reaction takes place on these metallic nanoparticles, therefore controlling their shape and size is of utmost importance.

Preparing catalysts is a time-consuming process as these are composite materials, in this case comprised of three major components. Iron oxide-based MNPs are embedded within a carbonaceous or an alumina matrix to serve as a support material for the aforementioned metallic NPs. We primarily focus on Ru and sometimes alloy it with Ni. Normally, various metals are deposited onto active carbon supports that do not feature any magnetic cores. The reason for including them is so they can be heated using an external AC magnetic field. Due to hysteresis losses, the support starts to heat up from the inside out. If prepared correctly, the temperature ramp-up is substantially faster than normal heating using, for example, a heating mantle positioned around the reaction vessel. Heat is then transferred to the catalytic particles and the reaction can proceed. Hypothetically, doing so increases energy yield. Furthermore, the induction coil does not need to be in immediate contact with the catalyst.

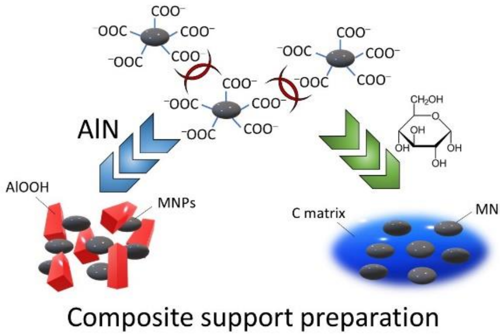

Figure 1. A schematic representation of composite support preparation from MNPs. The precursors require further processing.

**Acknowledgements**: We would like to thank for the financial support from the Slovenian research agency (research core funding Nos. P2–0089, P2–0152 and young researcher scheme contract No.1000-18-0106).

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# Defect-modulated catalytic response in 2D carbon nitride: insights from modeling

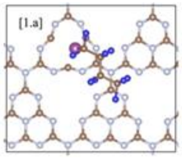
Edoardo Raciti,[1] Sai Manoj Gali,[2] Giacomo Filippini,[1] Michele Melchionna,[1] Paolo Fornasiero,[1] Maurizio Prato,[1] David Beljonne[2*] and Roberto Lazzaroni[2*]

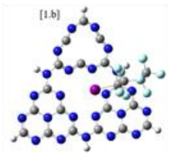
*david.beljonne@umons.ac.be; *roberto.lazzaroni@umons.ac.be

[1] *Department of Chemical and Pharmaceutical Sciences, Via Licio Giorgieri 1, University of Trieste, 34100 Trieste, Italy*
[2] *Faculty of Science, Mendeleïev Building, "Campus de la Plaine", Avenue Victor Maistriau 23, University of Mons, 7000 Mons, Belgium*

In the study that we are going to present here, some of us in the laboratory of Trieste had previously prepared some post-synthetic forms of carbon nitride[1], such as a richer $^1$H-containing one named as reduced (**red. g–CN**), an oxidized (**ox. g–CN**) and an irregular and disrupted one named amorphous (**am. g–CN**). These new materials were then employed as the photocatalysts of interest in a perfluoroalkylation reaction between 1,3,5-trimetoxybenzene and nonafluoro-1-iodobutane ($C_4F_9$–I) in presence of a 450 nm blue-light source, in dimethyl Formamide 0.4 M in inert atmosphere and carbon nitride's post-synthetic forms as the photocatalysts to test. Among the three, the amorphous showed the highest catalytic efficiency but despite the full physico-chemical characterization[2], the experimental conditions could not provide an explanation for the electron-transfer step supposed to occur from the catalyst to the molecule and why the amorphous form was responding more than the others.

For this purpose, Density Functional Theory was employed at a molecular and periodic approach. In order to extract electronic structures and Molecular Orbitals' energies (MOs), we initially optimized molecular models of possible carbon nitride's representations for all its post-synthetic forms. Analogously, we optimized periodic models, from which the correspondent electronic structures and band-gaps were extracted. We then built at both approaches combined gCN + $C_4F_9$ –I systems in order to determine, at the ground state, the interaction between the two, to then invoke Time-Dependent DFT to model the real photochemical reaction at the excited states. The system am. g–CN + $C_4F_9$ –I gave the lowest excitation energies required in the electron transfer[1] and the most delocalized MOs onto $C_4F_9$–I, this explaining the higher response of the amorphous form of carbon nitride.





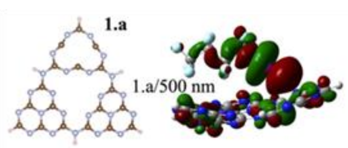


**Figure [1.a]**: periodic am. g–CN+$C_4F_9$–I system.
**Figure [1.b]**: molecular am. g–CN+$C_4F_9$–I system.
**Figure 1.a**: representation of the Molecular Orbitals involved in the electron transfer.

**Acknowledgements**: Belgian National Fund for Scientific Research, FNRS-PDR-TOREADOR project; the Consortium des Équipements de Calcul Intensif – CÉCI; Walloon Region (ZENOBE Tier-1 supercomputer); FRA2021 funded by the University of Trieste and Microgrants 2021 funded by Region FVG (LR 2/2011, ART. 4).

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# Towards composite hydrogels with functionalized carbon nanostructures and a self-assembling tripeptide

Petr Rozhin, Simone Adorinni, Alessandro Beltram, Daniel Iglesias and Silvia Marchesan*

*smarchesan@units.it

*Chemical and Pharmaceutical Sciences Department, University of Trieste, 34127 Trieste, Italy*

Despite many years of research, ideal biomaterials to address big challenges in medicine, such as tissue regeneration and cancer theranostics for combined early diagnosis and therapy, are yet to reach the clinic. The requirements they need to satisfy are many, from the physicochemical and biological point of view, and it is difficult to conceive that one chemical component will meet them all. Many scientists are thus studying the combination of various nanostructures with biomolecules to take advantage of working at the nanoscale and of using Nature's building blocks.[1, 2]

In particular, self-assembling short peptides are attractive biomolecules that can alleviate the daunting task of organizing molecules into macroscopic, yet nanostructured soft matter, such as hydrogels with tuneable properties.[3] However, their mechanical properties often limit applications in various areas of nanomedicine, whilst notable improvements and new properties can arise from the inclusion of carbon nanomaterials, and they include conductivity and self-healing ability.[4,5]

This work tackles the functionalization of oxidised graphene, carbon nanotubes, and carbon nanohorns to covalently attach a self-assembling tripeptide that gels at physiological conditions.[6] Each modification step is verified by several techniques, including thermogravimetric analysis, Raman and ATR-IR spectroscopies, and TEM microscopy. The final products are then combined with a further amount of self-assembling tripeptide and gelation is assessed by rheology to define the effects of carbon nanomorphology on the final materials. However, the different curvature and chemical structure of each type of nanocarbon is reflected in different levels of reactivity, which requires optimization of synthetic protocols, as will be described in the presentation to outline the challenges of adapting organic chemistry to carbon nanomaterials.

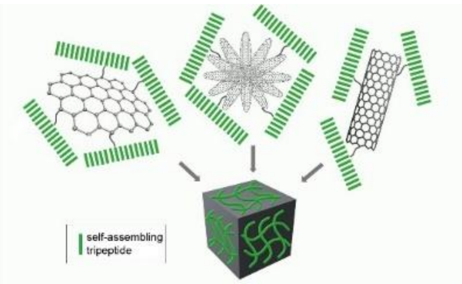

Figure 1. A self-assembling tripeptide is covalently attached to carbon nanostructures

**Acknowledgements**: The authors acknowledge MIUR for funding through the PRIN Giovani program (2015TWP83Z) and the COST Action EsSENce CA19118, supported by COST (European Cooperation in Science and Technology www.cost.eu).

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# The influence of molecular ordering on the cobalt phthalocyanine excited states dynamics

Cristian Soncini,[1,2] Abhishek Kumar,[1,2] Federica Bondino,[1] Elena Magnano,[1,3] Matija Stupar,[4] Barbara Ressel,[4] Giovanni De Ninno,[4,5] Antonis Papadopoulos,[6] Efthymis Serpetzoglou,[6] Emmanuel Stratakis[6] and Maddalena Pedio[1]

*cristian.soncini@phd.units.it

[1] *Istituto Officina dei Materiali, Consiglio Nazionale delle Ricerche, TASC Laboratory, Trieste, Italy*
[2] *Department of Physics, University of Trieste, Trieste Italy*
[3] *Department of Physics, University of Johannesburg, Johannesburg, South Africa*
[4] *University of Nova Gorica, Ajdovščina, Slovenia*
[5] *Elettra - Sincrotrone Trieste S.C.p.A, Trieste, Italy*
[6] *FORTH Institute of Electronic Structure and Laser Foundation for Research and Technology Hellas and University Of Crete, Hellas*

We present a multi-technique study on the impact of different structures on the dynamical electronic properties of cobalt phthalocyanine (CoPc) thin films. The CoPc relaxation dynamics in the ps time domain have been fully characterized by using transient absorption spectroscopy (TAS) (Figure 1a and b). We found that the charge transfer (CT) exciton lifetime in the herringbone α-phase (CoPc/Graphene sample) is enhanced with respect to the brickstone case (CoPc/Au(111) sample). Combined photoemission spectrosocpy (PES)- inverse photoemission spectroscopy (IPES) spectra clarify the molecular orbitals involved in the excited state dynamics. The complementary use of the information gained through TAS and time resolved PES (TR-PES) allows to single out a new dynamics involving an electronic state in the HOMO-LUMO gap (SOMO) with decay time of hundreds of fs (Figure 1c).

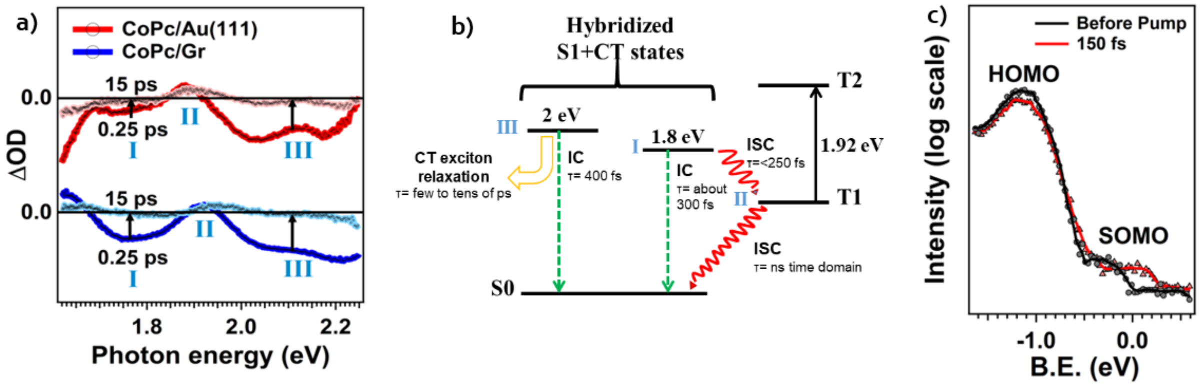

Figure 1: *a)* CoPc/Gr and CoPc/Au(111) TAS spectra in the Q-Band energy region*; b)* Jablonski diagram of the relaxation channels in the CoPc thin film (τ= decay time, S0/1 = singlet state, T1/2= triplet state, IC= internal conversion, ISC= intersystem crossing); *c)* CoPc/Au(111) sample TR-PES spectra before and after the 2 eV pump pulse.

# Triple-action nanoplatform for theranostic applications in hepatocellular carcinoma (HCC)

Aharon Steffè,[1,2]* Nicole Crestan,[1,3] Federica Di Cintio,[1,2] Monica Mossenta,[1,2] Davide Busato,[1,2] Idris Vruzhaj,[1,4] Paolo Macor,[2] Michele Dal Bo[1] and Giuseppe Toffoli[1]

*aharon.steffe@phd.units.it

[1] *Experimental and Clinical Pharmacology, Centro di Riferimento Oncologico di Aviano (CRO) IRCCS, Aviano, Italy*
[2] *Department of Life Sciences, University of Trieste, Trieste, Italy*
[3] *Department of Chemical and Pharmaceutical Sciences, University of Trieste, Trieste, Italy*
[4] *Department of Pharmaceutical and Pharmacological Sciences, University of Padova, Padua, Italy*

Hepatocellular carcinoma (HCC) is the most common type of liver cancer accounting for almost 90% of all cases. The staging and prognostic assessment of HCC is crucial for patients' management and HCC is classified into five stages ranging from very early to terminal, each of them related to different treatment options. To date, despite establishing screenings, many patients are diagnosed outside surveillance showing symptoms, which often relate to an advanced disease stage and dramatically limited possibilities[1]. Discovering new tumor-associated antigens (TAAs) for precision medicine and theranostic tools is needed to combine diagnosis and effective treatment of HCC patients. Glypican-3 (GPC-3) protein belongs to the family of heparan-sulphate proteoglycans. While not expressed on healthy adult liver tissue, it has a high expression on HCC cells, making it a promising TAA for HCC[2]. In the recent years, nanomedicine is emerged, and nanoparticles (NPs) are used to build multifunctional nanosystems with therapeutic and diagnostic abilities in several cancers[3].

We successfully developed and synthetized a hybrid nanoplatform composed of polymeric NPs (pNPs) made of poly(D,L-lactide-co-glycolide) (PLGA) and polyvinyl alcohol (PVA) with encapsulated gold NPs (GNPs) with two different sizes, 3-4 nm and 12-13 nm. NPs showed a size of 258.7 ± 28.4 nm for pNP_GNPs (12-13 nm) and 177.2 ± 16.0 nm for pNP_GNPs (3-4 nm), when analyzed by dynamic light scattering (DLS). They were stable at 25 and 37 °C, and over time up to 6 months. Furthermore, GNPs encapsulation was confirmed through transmission electron microscopy (TEM) and the concentration of entrapped gold were 0.27 ± 0.08 mg/mL for pNP_GNPs (12-13 nm) and 0.26 ± 0.01 mg/mL for pNP_GNPs (3-4 nm), as measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES). In addition, we demonstrated that all NPs were highly biocompatible *in vitro* on commercial cell lines with a cell viability decrease of 20% maximum. We also studied the NPs internalization through flow cytometry (FC) and laser scanning confocal microscopy (LSCM), showing a strong internalization efficiency after 24h. Currently, we are developing *custom-made* anti-GPC3 antibodies for the active cancer targeting (increased NPs accumulation in the tumor site) and testing our nanoplatform as contrast agent *in vitro* by ultrasound (US) imaging and synchrotron X-ray computed tomography (microCT).

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# Incorporation of vaginal lactobacilli into electrospun nanofibers: toward a new treatment of vaginal infections

Spase Stojanov,[1,2] Tina Vida Plavec,[1,2] Julijana Kristl,[2] Špela Zupančič,[2] and Aleš Berlec[1,2*]

*ales.berlec@ijs.si

[1] *Department of Biotechnology, Jožef Stefan Institute, Ljubljana, Slovenia*
[2] *Faculty of Pharmacy, University of Ljubljana, Ljubljana, Slovenia*

Vaginal infections are one of the most frequent health problems women face today. They are caused by dysbiosis of the vaginal microbiota, whereby the reduction of normal lactobacilli allows the growth of opportunistic pathogens, such as *Gardnerella vaginalis* and *Candida albicans*. Re-establishing the normal vaginal microbiota with probiotic lactobacilli can prevent the growth of the pathogens and stop the development of infections. However, the use of vaginal probiotics is hampered by the lack of appropriate delivery systems and the lack of tools for studying their functionality.

In our present work, we genetically engineered three vaginal lactobacilli, *L. crispatus*, *L. jensenii* and *L. gasseri*, as well as a control *L. plantarum*, to express fluorescent proteins with different spectral properties (GFP, mTagBFP2, mCherry and IRFP) which enable their analysis and visual identification in a mixture. The four species were successfully incorporated into polyethylene oxide (PEO) nanofibers, which are produced through electrospinning, a technique based on drying of a polymer solution in a strong electric field. Nanofibers represent a novel type of delivery system with large surface to volume ratio (1). Bacteria retained their fluorescence after incorporation and could be distinguished in the mixture based on their fluorescence (Figure 1) (2). Apart from pure PEO (4% (w/V)), PEO/alginate (4% (w/V); 80/20 ratio) and PEO/alginate/sucrose (8% (w/V); 40/10/50 ratio) were also used for the production of nanofibers, and viability was assessed before and after electrospinning through the course of 8 weeks. The three vaginal species, i.e. *L. crispatus*, *L. jensenii* and *L. gasseri*, retained viability after electrospinning, with *L. gasseri* demonstrating the highest viability (< 2 log decrease), followed by *L. jensenii* (< 3 log decrease), and *L. crispatus* (< 7 log decrease). *L. jensenii* in PEO and *L. gasseri* in PEO/alginate/sucrose retained viability after 8 weeks of storage. Our research is the first step towards the development of a new medicine against vaginal infections based on nanobiotechnology.

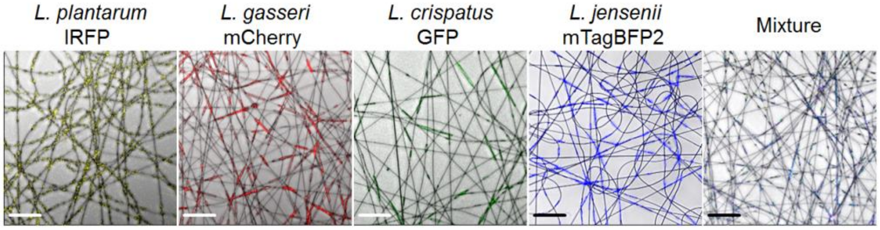

Figure 1. Incorporation of four fluorescent lactobacilli into electrospun nanofibers, individually or as a mixture.

**Acknowledgements**: This work was funded by the Slovenian Research Agency (P4-0127).

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# Study of CO oxidation on Pt atomic systems supported on $TiO_2$

Mina Taleblou*, Matteo Farnesi Camellone, Stefano Fabris, and Simone Piccinin

**mina.taleblou@phd.units.*it; mtaleblo@sissa.it

*CNR-IOM, Consiglio Nazionale delle Ricerche, Istituto Officina dei Materiali, c/o SISSA, Via Bonomea 265, 34136, Trieste, Italy*

The catalytic activity of small Pt clusters supported on brookite $TiO_2$ (210) was studied employing density functional theory (DFT) calculations. The specific catalytic reaction considered in this work is the oxidation of CO(g) into CO2(g), and it is simulated on different Pt clusters of different size and oxidation state. Our findings show that within the range of temperature (300~ 500 K) and CO pressure (0.2~ 0.8 bar), Pt clusters are partially oxidized and fully covered by CO molecules. Different approaches regarding oxidation of CO on Pt systems were investigated: Mars-Van Krevelen (MvK), Langmuir Hinshelwood (LH), and Eley-Rideal (ER). Our simulations predict that the oxidation of CO via MvK mechanism is thermodynamically favorable on both single Pt adatom and $Pt_6$ cluster, while the activation barrier of the reaction is larger on $Pt_6$. On the other hand, the highest activation barrier of CO oxidation is very similar on both Pt systems through LH mechanism. Further, CO oxidation is found to be more facilitated through ER mechanism on single Pt atoms substituting 6-coordinated Ti atoms of the supporting surface. Simulation of CO oxidation over an oxidized $Pt_6$ system predicts that during the reaction, the system will turn back to the metallic state.

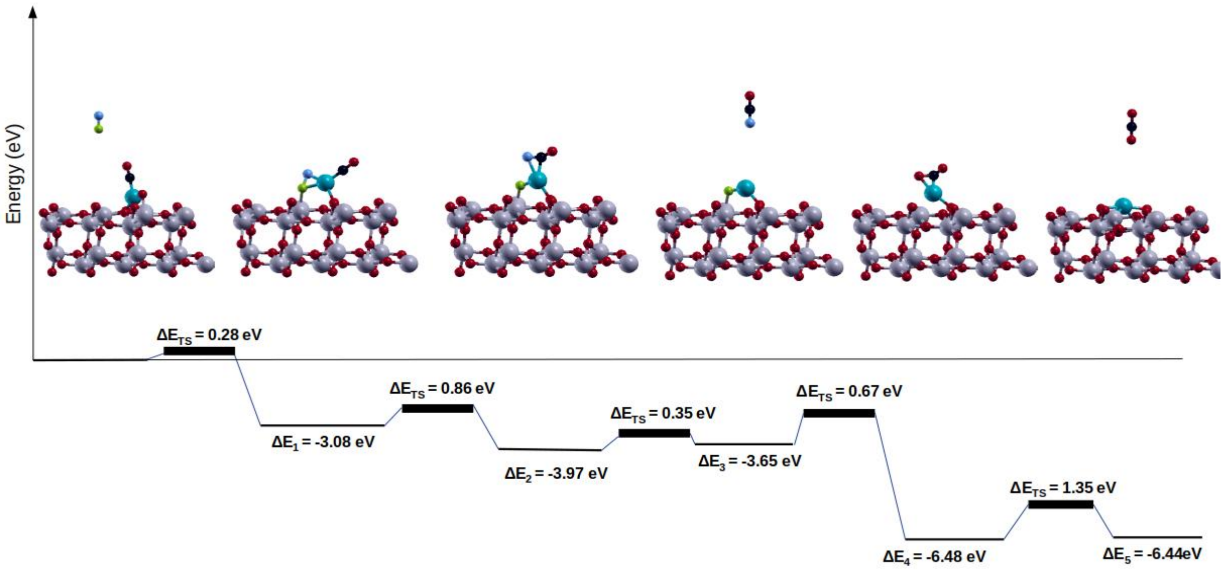

Figure 1. Full catalytic cycle of CO oxidation on $TiO_2$ supported single Pt atom.

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# Reduction of $CO_2$ to fuels by photocatalysis and electrocatalysis

Smritirekha Talukdar and Tiziano Montini

*smritirekha.talukdar@phd.units.it

*Department of Chemical and Pharmaceutical Sciences, University of Trieste, Via L. Giorgieri 1, 34127, Trieste, Italy*

With advancements in human lifestyle and consumption of fossil fuels, the amount of $CO_2$, a major greenhouse gas has been increasing in the atmosphere. Achieving clean energy along with subsequent reduction of such greenhouse gases is hence very important.[1] Thus, in addition to $CO_2$ capture and storage, converting it into simple hydrocarbon fuels is an effective strategy for solving the problem.[2] However, $CO_2$ being a very stable molecule with its linear geometry is difficult to undergo conversion demanding high energy input.[3] This work focuses on synthesizing effective catalysts using simple techniques like reflux and hydrothermal method to study the conversion of $CO_2$ to fuels by photocatalysis and electrocatalysis. Heterojunction-based catalysts with Z scheme interaction have been synthesized where effective tuning of band gap enhances the photocatalytic activity of the catalysts.[4] Nanocomposites based on g-$C_3N_4$ and metal oxides such as $Bi_2O_3$, $WO_3$, $CeO_2$ and oxychloride such as BiOCl have been synthesized. Characterization techniques such as SEM, TEM, and XRD were carried out to understand the size, morphology, and phases of the nanocomposites. $N_2$ adsorption/desorption isotherm showed increment in the specific surface area as compared to the pristine materials allowing increased adsorption of the gases for catalysis. Preliminary investigation of photocatalysis showed improved production of $H_2$ by $CeO_2$/g-$C_3N_4$ as compared to pristine g-$C_3N_4$. These nanocomposites were also tested for electrocatalytic reduction of $CO_2$. A three-electrode cell was set-up connected to a potentiostat workstation and an online GC. 0.1 M $KHCO_3$ was used as the electrolyte and the faradaic efficiencies were calculated after 60 mins of electrocatalysis for $HCOO^-$. 20% $Bi_2O_3$/g-$C_3N_4$ showed a high faradaic efficiency of 89.48% at -1.456V vs NHE whereas 0.05 CN/BiOCl showed a faradaic efficiency of 52.20% at -1.256V vs NHE. Trace amounts of gaseous products of H2 and CO were also detected through Gas Chromatography.

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# Chiral domains and charge density wave dynamics in 1T-TaS$_2$

Yevhenii Vaskivskyi,[1*] Jan Ravnik,[1,2] Jaka Vodeb,[1] Michele Diego,[1] Yaroslav Gerasimenko,[3] Viktor Kabanov,[1] Andrej Kranjec,[1] and Dragan Mihailovic[1,3]

*yevhenii.vaskivskyi@ijs.si

[1] *Complex Matter Department, Jozef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia*
[2] *Laboratory for Micro and Nanotechnology, Paul Scherrer Institut, Forschungsstrasse 111, 5232 Villigen PSI, Switzerland*
[3] *Center of Excellence on Nanoscience and Nanotechnology – Nanocenter (CENN Nanocenter), Jamova 39, SI-1000 Ljubljana, Slovenia*

1T-TaS$_2$ is well-known for its metastable low-temperature hidden-state[1] in which charge density wave (CDW) forms domains and domain walls. At equilibrium conditions, CDW in the material exists in only one two-dimensional symmetry on a scale of tens of micrometers. On the other hand, non-equilibrium conditions can cause not only the appearance of domain walls but also chiral domains (of left- and right-handed symmetry, Fig. 1a). As a result, both chiralities can be observed and studied on a scale of only tens of nanometers.

Using scanning tunneling microscopy we investigate the dynamics of these L- and R-handed domains at 4 K and 77 K after illumination using 50 fs 800 nm laser pulses. Even though domain structure is stable at low temperatures, the coexistence of two chiralities results in a small amount of spontaneous relaxation in the domains. Moreover, such coexistence can lead to the formation of the domains where both symmetries are observed at the same time, resulting in "flower-shaped" interference patterns (Fig. 1b).

In this work, we are showing that usage of scanning tunneling microscopy allows us to study the local dynamics of a charge density wave in 1T-TaS$_2$ after undergoing non-equilibrium conditions. Using this top-layer sensitive technique, we show that the symmetry and observed CDW patterns can be understood as a superposition of L and R states, leading to the new knowledge of 1T-TaS2 properties.

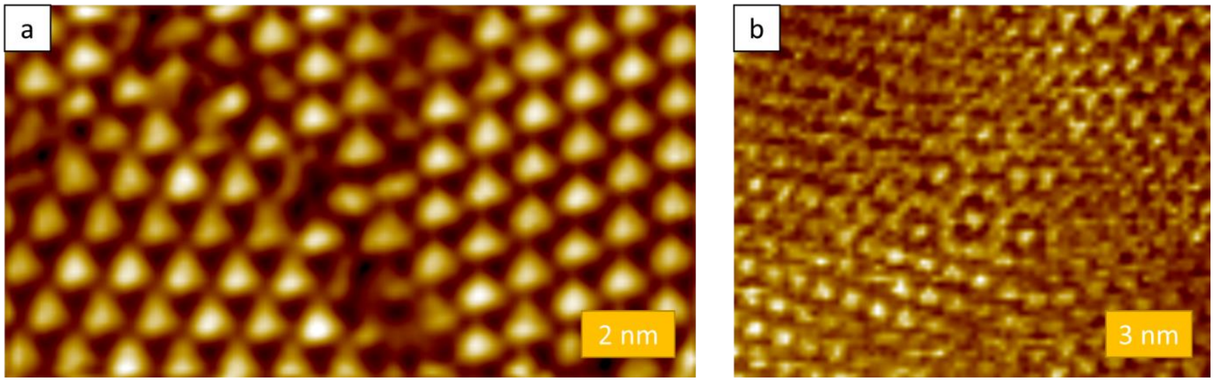

Figure 1. a) Left- and right-handed domains in 1T-TaS2 with a domain wall in-between. b) "Flower-shaped" patterns (in the center) of two-chirality interference in the region of L and R coexistence.

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# Cardiac tissue models to investigate the heart mechanobiology

Michele Zanetti,[1,2]* Laura Andolfi,[2] Erik Betz-Guttner,[1,2] Emre Coşkun,[3,4] Alpan Bek,[4,5] Matthew R.G. Taylor,[6] Luisa Mestroni[6] and Marco Lazzarino[2]

*zanetti@iom.cnr.it

*[1] Department of Physics, University of Trieste (Trieste, Italy)*
*[2] CNR-IOM Istituto Officina dei Materiali (Trieste, Italy)*
*[3] Department of Physics, Çanakkale Onsekiz Mart University (Çanakkale, Turkey)*
*[4] ODTÜ-GÜNAM Center for Solar Energy Research and Applications (Ankara, Turkey)*
*[5] Department of Physics, Middle East Technical University (Ankara, Turkey)*
*[6] University of Colorado Denver, Anschutz Medical Campus (Aurora, CO, USA)*

Cardiovascular diseases (CVDs) are the leading cause of death worldwide. One of the main issues in post-myocardial infarction recovery is the inability of the heart to rebuild a functional syncytium. Indeed, the damaged myocardium is replaced by a fibrotic scar, which leads to improper mechano-electrical compliance. Many approaches to limit this pathological deterioration are currently under investigation. Yet, our understanding of the myocardial rheology is insufficient, partially because we lack the appropriate techniques to model it. We create Cardiac Spheroids (CS) mixing neonatal rat cardiomyocytes (NRCMs) and fibroblasts in definite ratios. We study the viscoelasticity of such models using Atomic Force Microscopy (AFM), using custom-fabricated "macro-cantilevers" to overcome the size limitations imposed by commercial probes. We observe different relaxation times within different culture conditions and cellular composition. Moreover, by applying cyclic mechanical loads, we stimulate the CS contractions as for a "micro" heart massage. This paves the way towards a finely tuned mechanical stimulation, which has been shown to increases cardiomyocytes matureness by activating hypertrophic pathways[1]. Parallelly, electrical field stimulation can boost contractile performance, too[1]. For this, cell-cell interconnections (i.e., gap junctions) must be sufficiently mature and ubiquitous to propagate the electrochemical flow. Artificial nanomaterials such as carbon nanotubes can instruct such biological duty by providing electrical shortcuts in electroactive cells[2].

Moreover, cardiomyocytes grown together with Silicon Nanowires (SiNWs) exhibit higher expression of connexin-43 and a superior maturation degree[4]. To investigate their contractile properties in this framework, we culture immature NRCMs (P1-3) together with trace amount of SiNWs (ø ~ 100 nm, L ~ 2 μm, 0.004% w/v) and we perform single-cell AFM mechanocardiogram using a sharp probe after three days of culture. We observe the SiNWs partially entering the plasma membrane and interacting with the nuclear boundary as shown by SEM imaging. Hopefully, these findings will guide us towards a more comprehensive picture of the cardiomyocyte mechanodynamics in both physiological and pathological conditions.

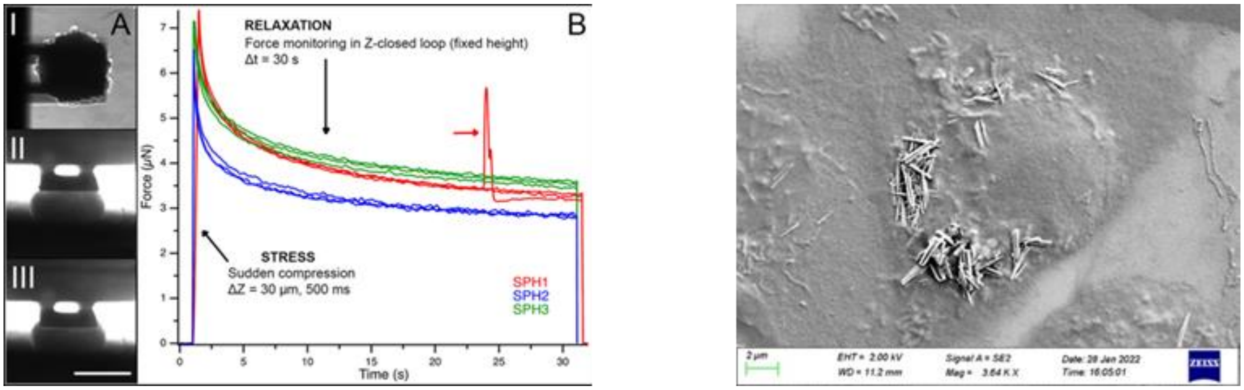

Figure 1 (left) A. Optical images of a CS under a macro-cantilever. (I) Bottom view. (II) Before compression (III) After compression. Scalebar: 300 µm. B: AFM stress-relaxation curves, after baseline subtraction. SPH1 shows contractility (red arrow) at ~ 25 s. (right) SEM micrograph of a cell integrating SiNWs in its plasma membrane.

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# On the role played by protein-asbestos fiber interaction in asbestos toxicity: a multi-technique approach from single fiber to cellular and tissue milieu

Martina Zangari,[1,2] Federica Piccirilli,[2] Annalisa Bernareggi,[1] Giuliano Zabucchi[1] and Lisa Vaccari[2*]

*lisa.vaccari@elettra.eu

[1] *Department of Physics, University of Trieste, Via Valerio 2, 34127 Trieste, Italy*
[2] *Elettra-Synchrotrone Trieste S.C.p.A.*

In the past century asbestos, a natural mineral, was used because of its resistance and low-cost[1]. However, its proven harmfulness to health has led to its use being banned in many countries, including Italy. Respiratory exposure to asbestos fibers is a hazard to human health, because their inhalation is associated with severe lung diseases such as asbestosis, pleural mesothelioma and lung cancer[2]. A peak of mortality of many thousands of exposed subjects is predicted for the next 10 years. Until now, the process of fiber entry into the cells, its interaction with membrane proteins and the effects induced by these events on cell physiology (cell proliferation and oxidative stress) are only some of the topics which wait to be fully understood[3]. The comprehension of the mechanisms of interaction of asbestos fibers with cells is of fundamental importance to clarify the pathogenetic pathways of these diseases and to set up specific therapeutic approaches for the treatment of exposed subjects. One key process in the pathogenesis of asbestos induced diseases, is the interaction of fiber with proteins: it can trigger the entry in the cytosol, can induce cytoskeleton modification and apoptosis. Many proteins are able to bind to the asbestos fibers, including ferritin[3], RNA-binding proteins, cytoskeletal proteins, ribosomal proteins[4], ion channel proteins, such as TMEM16A. The association protein-fiber can induce a significant increment of the enzymatic activity, which may be possibly induced by a structural modification of the absorbed protein[5]. In the lung tissue, protein-asbestos fiber interaction is shown in the formation of asbestos bodies (AB), (asbestos fiber coated with mucopolysaccharides and iron containing proteins[6].
The project intends to study the protein structural modifications after the fiber interaction with FTIR microscopy and biochemical techniques. In particular, we set up a protocol to reproduce AB model *in vitro* composed by (apo/holo) ferritin and chrysotile using three different pH (7.0 cytoplasmic, 5.0 and 8.0 phagosome). The results show that our procedure is a good method to reproduce AB model *in vitro*. The FITR microscopy analysis revealed that, after chrysotile incubation, (apo/holo) ferritin undergo a strong change of secondary structure: native proteins have a prevalent $\alpha$-helix structure, while in the AB model, they show a prevalent B-sheet and turn structure.

**Acknowledgements**: We would like to thank Bedolla D., Leone S., Zacchi P. and Borelli V. for their precious contribute.

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# Toxicological research: labelled microplastics detection in an *in vitro* human model by soft X-Ray Micro-Spectroscopy

Federica Zingaro,[1,2*] Alessandra Gianoncelli,[2] Lorella Pascolo[3] and Giacomo Ceccone[4]

*federica.zingaro@phd.units.it

[1] *Physics Department, University of Trieste, 34127 Trieste, Italy*
[2] *Elettra – Sincrotrone Trieste, Area Science Park, 34149 Basovizza, Trieste, Italy*
[3] *Institute for Maternal and Child Health, IRCSS Burlo Garofolo, 34137 Trieste, Italy*
[4] *European Commission, Joint Research Centre, Institute for Health and Consumer Protection, 21027 Ispra (VA), Italy*

The environment is contaminated with numerous pollutants, such as heavy metals, microplastics (MPs), perfluorinated organic compounds, and pesticides, which toxicity and harmful impacts on human health presents a critical emerging area for research.

To start investigating this, we propose model MPs made of the three most common polymers (polyethylene, polypropylene, polyvinyl chloride), labeled with cadmium-selenide quantum dots, semiconductor nanocrystals and characterized by unique optical properties, to provide new data on cell-MPs accumulation and toxicity, using synchrotron radiation X-ray imaging combined with fluorescence micro-spectroscopy (TwinMic, ELETTRA Sincrotrone, Trieste). The present approach overcomes the standard optical techniques' limitations (precise metal detection, semi-quantifications) by providing simultaneously morphological information and elemental correlations at sub-cellular spatial resolution and higher sensitivity.

While aiming to investigating the innate immune responses to MPs, acting as non-self-agents in humans, the monocyte-to-macrophage differentiation *in vitro* model is exploited: THP-1, human monocytic cell line, is grown in complete culture medium onto the appropriate substrates for X-Ray analyses, differentiated into M1, the pro-inflammatory phenotype, by incubation with phorbol 12-myristate 13-acetate, polarized with IFN-γ and LPS, and incubated with QDs-PE, PP-, PVC- MPs (50-350 nm sized) for 72 hours.

Fluorescence microscopy helped to localize QDs-MPs (Fig.1a) in cells to be mapped at TwinMic beamline. Every MPs type was detected in the exposed macrophages by X-Ray fluorescence microscopy by tracking the emission of Se L-line of QDs (Fig.1b) confirming their internalization in accordance with fluorescent images. XRF results did not reveal substantial alteration in the light elements (Na, O) distribution. Absorption and phase contrast maps revealed the accumulation of lipid droplets, LDs, (Fig.1c) within macrophages in response to PP-MPs, which is a specific oxidative stress response and a metabolic feature of phagocyte activation. LDs can lead to the formation of foam cells, by secreting various substances such as cytokines, involved in inflammatory pathways to pathogenic hazards, such as pollutants. However, PE- and PVC- MPs, induced detachment of cells' structures, being less tolerated, require further sampling and characterization.

Evaluating the uptake mechanisms and cell responses to MPs, taking advantages of advanced analytical techniques represents an important approach to assess the toxicological accumulation of pollutants in human organisms.

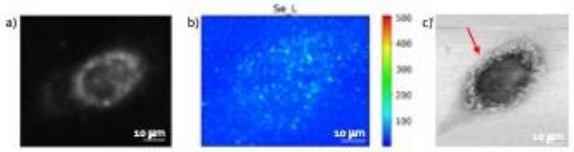

Figure 1. a) Fluorescence image of a M1 cell exposed to CdSe QDs-PP-MPs with Texas Red filter; b) Se_L LEXRF map of the same cell of panel a; c) absorption image acquired at 1.7 keV with 300 nm spatial resolution.

**Acknowledgements**: This project is supported by the Central European Research Infrastructure Consortium (CERIC).