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Chiral Carbon Dots: towards stereoselective nano-catalysts

Beatrice Bartolomei,¹ Vasco Corti,¹ and Maurizio Prato^{1,2,3*}

*prato@units.it

¹ Department of Chemical and Pharmaceutical Sciences, INSTM UdR Trieste, University of Trieste, Via Licio Giorgieri 1, 34127 Trieste, Italy

² Center for the Cooperative Research in Biomaterials (CIC BiomaGUNE), Basque Research and Technology Alliance (BRTA), Paseo de Miramón 194, 20014, Donostia San Sebastián, Spain

³ Basque Fdn Sci, Ikerbasque, 48013 Bilbao, Spain

Carbon dots (CDs) are carbon-based materials that have recently gained great interest both for their luminescent properties and rich-surface chemistry which make them very promising for the development of metal-free nano-catalytic platforms.¹⁻³ The bottom-up approach is a versatile methodology for the preparation of CDs. Indeed, the appropriate selection of starting materials, doping agents, and synthetic conditions affords nanoparticles with tailored structural and optical properties.⁴ Leveraging on our expertise in the preparation of CDs, we have engineered new chiral nanoparticles. Our approach consists in a one-pot microwave-assisted hydrothermal synthesis, using citric acid and either (*S*)-2-(Aminomethyl)-1-Boc-pyrrolidine or its (*R*)-enantiomer. The so-obtained materials present a broad absorption and emission in the visible region of the spectrum and their chirality is confirmed by specular circular dichroism spectra. The presence of functional groups on the surface and the light-absorbing properties of our CDs have paved the way for their exploitation as recyclable nano-catalysts. In particular, in this work we have investigated their use as organocatalysts to drive asymmetric reactions and as photocatalysts in Atom Transfer Radical Additions (ATRA). Building on these results, we employed the developed CDs as combined photo-organocatalytic systems to drive a cross-dehydrogenative coupling under visible light irradiation. In this scenario, the carbon-based nanoparticles were used to photogenerate reactive radical species in solution that can be trapped by the organocatalytic intermediates (e.g., enamines) on the surface of CDs. This methodology may lead to the development of simple, chiral and reusable nano-sized photo-organocatalysts where the advantages of both the nanoscale and the molecular fields are merged and complemented by each other.

Acknowledgements: This work was supported by the European Research Council (ERC AdG-2019 n° 885323, e-DOTS) and the University of Trieste.

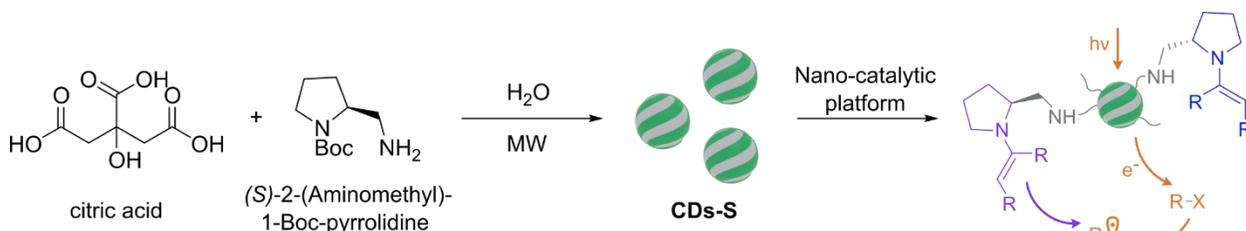


Figure 1. General scheme for synthesis and catalytic applications of chiral CDs.

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The surface reactivity of A site-doped SrTiO₃: an ambient pressure NEXAFS experiment

Ferdinando Bassato,^{1,2*} Silvia Mauri,^{1,2} Alexander Petrov,² and Piero Torelli²

*ferdinando.bassato@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

In the last few years, research on solid oxide fuel cells (SOFCs) has increased considerably and SrTiO₃-based perovskites turned out to be promising anodes for SOFCs, provided that a suitable doping is performed^{1,2}. In this framework, we investigated with *operando* NEXAFS the surface reactivity of SrTiO₃-thin films (La_{0.2}Sr_{0.7}TiO₃ (LSTO) and La_{0.2}Sr_{0.25}Ca_{0.45}TiO₃ (LCSTO)) grown with Molecular Beam Epitaxy. The measurements were performed at APE-HE beamline (Elettra Sincrotrone, CNR-IOM) exploiting the NEXAFS reaction cell developed *ad hoc*³. The samples were exposed to a reducing atmosphere (He/H₂, 50 %) at 400°C and LCSTO displayed a notably higher amount of Ti(III) than LSTO, thus confirming the positive effect of co-doping to lower the activation temperature of the material. Moreover, we synthesize by hydrothermal route the same samples previously grown by MBE because we envisaged that the chemical synthesis, bearing the presence of point defects and porosity, could provide an enhanced surface reactivity of the catalyst with respect to the reference MBE films. In fact, the NEXAFS spectra of the powders revealed a higher amount of Ti(III) than the corresponding MBE films, as well as a reduced t_{2g} - e_g energy gap, hinting that also structural modifications may take place. We think that these experiments could provide remarkable insights on the electronic structure of these catalysts at real working conditions.

Acknowledgements: NFFA-MIUR and Elettra Sincrotrone are gratefully thanked for the support. This work is included in the framework of "Programma Operativo Nazionale (PON), Ricerca e Innovazione 2014-2020".

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A study inside the catalytic behavior of Cu₂O nanoparticles

Matteo Bisetto,¹ Alberto Naldoni,^{2,3} Tiziano Montini,¹ and Paolo Fornasiero¹

matteo.bisetto@phd.units.it

¹Dipartimento di Scienze Chimiche e Farmaceutiche, 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 nanostructuring 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 (Cu₂O) nanocrystals got huge attention due to their unique facet dependent properties³. Being cheap and earth abundant, such well-defined Cu₂O nanostructures can be used as catalysts for the electrocatalytic CO₂ reduction reactions thank to the high reactivity toward C-C bonds formation. However, the low stability of Cu₂O and the poor selectivity limits the industrial applications of this material⁴.

In this project, pristine Cu₂O nanoparticles (Cu₂O NPs) with a tailored shape had been synthesized via a wet-chemical route. Two structures were chosen: cubic (CU-Cu₂O) and Rhombo-Dodecahedral nanoparticles (RD Cu₂O). The electrocatalytic behavior of the pristine materials had been studied in a gas-tight electrochemical cell, evidencing a poor selectivity toward the different CO₂RR products and similar activity between the two chosen shapes. To unveil the reasons of this similar behavior, *in operando* XANES had been performed during the electrochemical CO₂RR experiments, unveiling an instant conversion of the material to Cu (0). To solve this problem, different efforts were focused on the formation of different composites with Cu₂O and the study of their electrocatalytic properties. Indeed, formation of heterojunctions is one of the main solutions to contrast the very low stability of cuprous oxide and simultaneously, to enhance the selectivity of the catalyst⁴. In particular, Cuprous oxide had been coupled with nanostructured materials such as g-C₃N₄, Reduced Graphene Oxide (RGO) and MoS₂. The synthetic procedure allows the formation of heterostructures with a rational choice of the weight fraction, an easy control of the final shape of Cu₂O and, mainly, a decreasing of the average sizes of the nanoparticles.

The formation of heterostructures is directly correlated to an improved selectivity towards CO₂RR products, mainly CO (for the composite with RGO) and formates (for the heterostructure with g-C₃N₄), and the use of different electrochemical setups allows to explore more industrial applications for these catalysts.

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Synthesis and characterization of nanostructured carbon horns for the electrochemical water splitting

Andrea Bogo,^{1,*} Michele Cacioppo,^{1,2} and Maurizio Prato^{1,2,3}

*ANDREA.BOGO@phd.units.it

¹ Department of Chemical and Pharmaceutical Sciences, INSTM UdR Trieste, University of Trieste, via Licio Giorgieri 1, 34127 Trieste, Italy

² Centre for Cooperative Research in Biomaterials (CIC biomaGUNE), Basque Research and Technology Alliance (BRTA) Paseo de Miramón 194, 20014 Donostia San Sebastián, Spain

³ Ikerbasque, Basque Foundation for Science, 48013 Bilbao, Spain

Electrochemical water splitting, promoted by renewable sources, is one of the most promising processes to achieve the carbon-neutral economy.¹ However, the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) have a very sluggish kinetic. Both of the reactions require noble metals and the sustainability of the process is dependent on the abundance of these precious metals. In this context, we propose the development of new electrocatalysts based on nanocarbons and metallic nanostructures. The catalysts are being designed by a combination of Nickel nanoparticles (NiNPs) and Ruthenium polyoxometalates (Ru₄POM) loaded onto carbon nanohorns (CNHs).² The latter material consists on closed cages of sp²-carbon atoms forming a multi-conical structures with fullerene-like tips.^{3,4} The CNHs provide the conductivity and surface area, working synergistically with the reaction centers for HER and OER: NiNPs and Ru₄POM respectively. At this stage of the work, research activities have been focused on the functionalization or modification of CNHs. In the first case NiNPs deposition on CNHs has been achieved (Ni/ox-CNHS), while in the second case nitrogen-doped CNHs (N-CNHS) were produced for future experiments on Ru₄POM anchoring.

The Ni/ox-CNHS were produced by a *in situ* NiNPs deposition through a solvothermal process. The products were characterized by Raman spectroscopy, TEM, XPS, TGA, FT-IR and ICP-MS confirming the fine deposition of Ni onto CNHs surfaces. N-CNHS were produced by nitrogen-doping synthetic solvothermal protocols, involving nitrogen containing precursors, in order to insert positively charged anchors point for interaction with the negatively charged Ru₄(POM).⁵ The nitrogen doping was demonstrated by Raman spectroscopy, FT-IR and XPS. The usefulness of N-doping for the interaction with Ru₄(POM) was provided by zeta potential (ZP). Indeed the ZP measures under pH 4 displayed a positive charged material. Encouraged by such positive results, novel typologies of nitrogen functionalization are being tested in order to optimize the positive charge on CNHs surfaces.

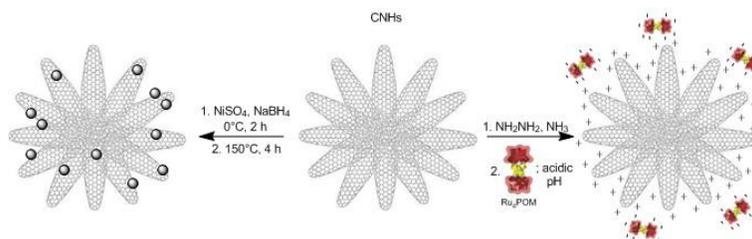


Figure 1. Schematic representation of CNHs functionalization strategies for HER and OER applications.

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Piezo1 channel investigation in cardiac fibrosis precursor cells mechano-physiology

Nicoletta Braidotti^{1,2,*}, Giorgia Demontis,^{1,2} Laura Andolfi,² Orfeo Sbaizero,³ and Dan Cojoc²

*nicoletta.braidotti@phd.units.it

¹ Department of Physics, University of Trieste, Via A. Valerio 2, 34127 Trieste, Italy

² Institute of Materials, National Research Council of Italy (CNR-IOM), Area Science Park Basovizza, Strada Statale 14, Km 163,5, 34149 Trieste, Italy

³ Department of Engineering and Architecture, University of Trieste, Via A. Valerio 6/A, 34127 Trieste, Italy

Cardiac stresses in dysfunctional myocardium can induce progressive cardiac remodeling leading to heart failure (HF) which basically consists in the loss of cardiomyocytes and fibrosis [1,2]. At the base of fibrosis an activation process involving fibroblast cells takes place. These cells undergo a phenotypic transition into muscle-like cell type called myofibroblasts becoming responsible for the progressive stiffening of the myocardium [1]. A positive feedback loop for myofibroblasts sustainment is then established, for which a fully interpretation about the leading pathophysiological fibrotic mechanisms is still missing. However, the discovery of the mechanosensitive Piezo1 channel in 2010 [3] opened a new pursuable way of investigation highlighting a possible interaction of this mechanically activated calcium channel in the mechanotransduction events occurring in the fibrotic process [4].

In this study, the response of primary rat cardiac fibroblasts to mechanical stimulations was investigated. Forces from piconewton to 350 nN were applied by exploiting Optical Tweezers and Atomic Force Microscopy, while monitoring intracellular calcium by calcium imaging. After 24 hours, a significant response was observed at a pressure of 3.8 kPa with a percentage of 11.43 % responding cells, which increased up to 60 % with 8.9 kPa pressure. Since it was demonstrated that fibroblasts begin to undergo phenotypical changes after one day culturing [5,6], the same experiment was performed after 48 hours of plating. In this case a lower percentage of cells responded to a similar mechanical stimulation, although the trend in the response with increasing pressure was maintained.

The stiffness of primary cardiac fibroblasts at 24 h and 48 h did not change significantly and as result the cell mechanics is not directly involved in the different mechanotransduction behavior.

To evaluate the involvement of Piezo1 in the response of primary cardiac fibroblasts to the applied pressure, cells were cultured with Yoda-1, specific activator of Piezo1, for 24h and then mechanically stimulated with same pressures. Preliminary experiments showed an increased percentage of responsive cells in the pressure range of 3-9 kPa.

The expression and location of Piezo1 channel at 24 h, 48 h culturing and after Yoda-1 co-culturing is investigated by qPCR and immunofluorescence imaging.

These results suggest a principal role of Piezo 1 channel in the response of primary cardiac fibroblast to mechanical variations of the microenvironment.

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Charge dynamics in complex 2D heterostructures

Claudio Lentini Campallegio

claudio.lenticinacampallegio@phd.units.it

¹ *Dipartimento di Fisica, Università degli Studi di Trieste*

I present the synthesis of trimers of Pyrene-1-Boronic Acid (PBA) on top of the Au (111) surface, and their characterization by means of XPS, UPS, NEXAFS and RESPES spectroscopy and STM microscopy.

The creation of organic-based electronic devices is an important and extensively studied application for organic molecules, with a particular interest in their interaction with metal and inorganic semiconductors. Specifically, molecules based on extended aromatic structures are interesting in a range of optoelectronic applications because of the capability of their π core to absorb Near-UV and visible light.

In my research, I studied trimers of pyrene-1-boronic acid, a pyrene that presents a $B(OH)_2$ substituent. These trimers result from a self-condensation reaction where three boronic acid group react to form a six-member ring structure constituted of alternating B and O atoms. This trimeric derivative was chosen because presents higher stability on on the Au(111) and other metal surfaces compared to the monomer. Furthermore, previous studies have demonstrated that the central B_3O_3 ring, known as boroxine ring, presents ultra-fast delocalization channels towards the Au(111) surface [1], resulting in possible applications of this molecules in the creation of electron transporting films.

The molecule was treated thermally in a quartz crucible, up until 290 °C, to allow the condensation reaction directly in the crucible, and the so-created trimers were evaporated on top of the Au(111) surface in UHV conditions. The resulting material was then analyzed using XPS, UPS and NEXAFS, and RESPES spectroscopy, pump-probe spectroscopy and STM microscopy.

The XPS demonstrated that B, O and Carbon where present on the surface, and showed a B:O ratio of around 1:1, compatible with the formation of boroxine rings. The B_{1s} NEXAFS analysis revealed three main π components, that is in agreement with the DFT calculation for boron involved in boroxine rings. The STM imaging showed that the trimers are organized into a ordered, platelet-like structure, on top of the Au(111) structure.

The RESPES measurements allowed for a chemical assignment of the electronic states of the valence band. Interestingly, the analysis of the resonant Auger signal reveals the presence of super-Participant decay process, which is related to an electronic coupling with the substrate, in terms of dynamic charge transfer from it.

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Co incorporated in graphene – a stable single atom catalyst

Valeria Chesnyak,^{1,2,*} Daniele Perilli,³ Mirco Panighel,² Alexander Markevich,⁴ Thi Thuy An Bui,⁴ Jani Kotakoski,⁴ Aldo Ugolotti,³ Alessandro Namar,¹ Giovanni Comelli,^{1,2} Cristiana Di Valentin,³ and Cristina Africh²

*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 Department of Materials Science, University of Milano-Bicocca, via R. Cozzi 55, 20125 Milano, Italy

⁴ Physics Department, University of Vienna, Boltzmannngasse 5, 1090 Wien, Austria

Single atom catalysts come in various systems with one main limitation, namely, the lack of stability.¹ In this context, graphene as a stable support, doped with heteroatoms, is one of the most promising materials ensuring the persistence of the single atom. Among possible metal dopants, Co plays a prominent role, as DFT calculations predict a significant effect of Co incorporation on both graphene's catalytic and magnetic properties.² Yet, no scalable method was reported to incorporate metals into the graphene mesh. Based on our previous research on understanding the Co-Ni-C system³, this study presents a bottom-up approach used to grow homogeneous and flat Co-doped graphene layers on Ni surfaces that are stable up to graphene dissolution temperatures. Their structure and reactivity were investigated by scanning tunneling microscopy (STM), scanning transmission electron microscopy (STEM), electron energy loss spectroscopy (EELS) and theoretical calculations. The existence of Co dopants beside Ni is proved by EELS spectra on incorporated atoms in collaboration with the University of Vienna. Moreover, selective adsorption was observed by in-situ gas exposure in the STM to O₂, CO and CO₂. The Co single atoms are interacting with the gases at room temperature in such a way that a more complex and dissociative process for CO₂ and O₂ is indicated. Therefore, this system has an outstanding potential to enable the investigation of the properties of single Co atoms and a fundamental insight into the dissociation process of simple gas molecules at room temperature.

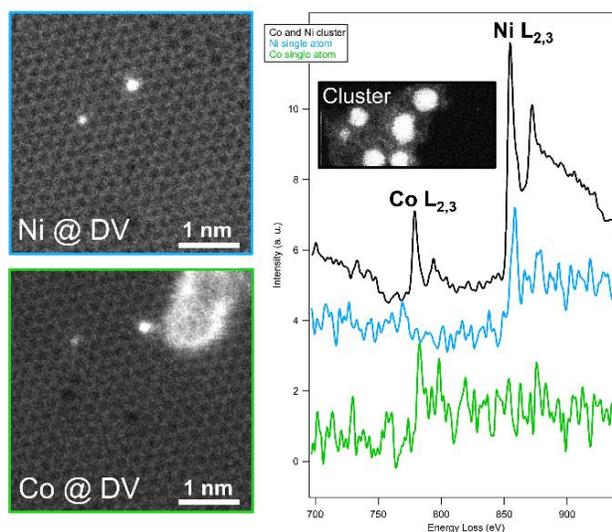


Figure 1. STEM images and EELS measurements of Co and Ni single atoms embedded in graphene in a double vacancy (DV). The inset in the EEL spectrum shows the image of the clusters for the reference signals of the L_{2,3} edges of Co and Ni.

Acknowledgements: This work has been supported by the Italian Ministry of Education, Universities and Research (MIUR) through the program PRIN 2017 - Project no. 2017NYPHN8.

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Imaging and analysis at nanoscale. Merging between SPM and optics

Filippo Costa,¹ and Stefano Prato²

*FILIPPO.COSTA@phd.units.it, stefano.prato@aperesearch.it

¹ Department of Physics, University of Trieste, via Valerio 2, 34127 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.

Part of this work focuses on the study of SLNPs and the dye indocyanine green (ICG) through Raman spectroscopy. We used the Scanning MicroRaman system provided by A.P.E. Research. To increase the resolution of the device I worked with the A.P.E. Research technicians. We modified the laser system to obtain a smaller spot. Reducing the size of the spot makes it possible to record spectra for smaller areas. Hyperspectral images of histological section of mice tissue were successfully obtained. From the results of the Scanning MicroRaman analysis we decided to use A.P.E. Research TriA-SNOM (scanning near-field optical microscopy) due to the strong fluorescence shown by the nanoparticles bound to the ICG dye. We've developed a system with three fibre-coupled lasers. To investigate the influence of fluorescence we interfaced the optical fiber of the SNOM with a spectrometer. Another upgrade on the SNOM allows us to see the possible fluorescence of the sample through the instrument's inverted microscope thanks to the insertion of a filter system. A special device has been built to switch between PMT and the inverted microscope camera. Thanks to this upgrade we were able to significantly reduce the time taken for the analysis.

After the update of the A.P.E. Research TriA-SNOM, we investigated the resolution of the new system on biological samples. With the final setup, we successfully obtain images with a resolution of about 100nm. This prototype, after optimization and appropriate development, will help to understand whether and in which tissue the NPs are taken up by the organism and thus make an important contribution to studies in the field of "drug delivery".

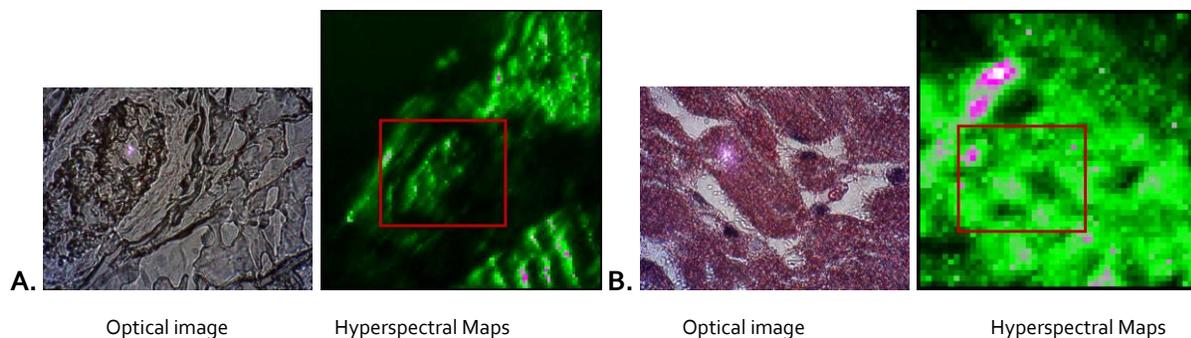


Figure 1. Mice thin section without (A) and with (B) dye (dye 190014-1). Scanning Hyperspectral Maps. Laser: 785 nm. Dimension: 200 x200 μ m.

Design, synthesis and applications of gold nanoparticles protected by fluorinated ligands as nanoplatform for imaging and drug delivery

M. Cretella,^a L. Pasquato,^a and P. Pengo^{a,*}

*matteo.cretella@phd.units.it

^a Università di Trieste, Dipartimento di Scienze Chimiche e Farmaceutiche, via Licio Giorgieri 1, 34127 Trieste (TS)

Small and monodisperse gold nanoparticles (AuNPs) protected by self-assembled monolayer (SAM) of tailored fluorinated thiolates were synthesized as contrast agent for ¹⁹F 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 in water and biocompatibility, a long linear perfluoro(polyethylene glycol) chain with a high number of (quasi)equivalent fluorine atoms for a single and intense ¹⁹F signal and a short mercaptoalkyl chain to link the compound to the gold core for increased system stability. AuNPs were synthesized 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 assessed by measuring T₁ and T₂ relaxation times and by conducting ¹⁹F phantom experiments, which are promising. To investigate the possible applications of AuNPs as drug carriers, ESR spectroscopy was employed to study the affinity of a hydrophobic probe, simulating a hydrophobic drug, for the AuNPs' monolayer. The binding constant that was determined by ESR is the highest measured compared to other SAM protected Au NPs. These properties make these fluorinated Au NPs particular promising nanomaterials both for drug delivery and imaging. Biological tests are in progress to evaluate the biocompatibility of these fluorinated NPs.

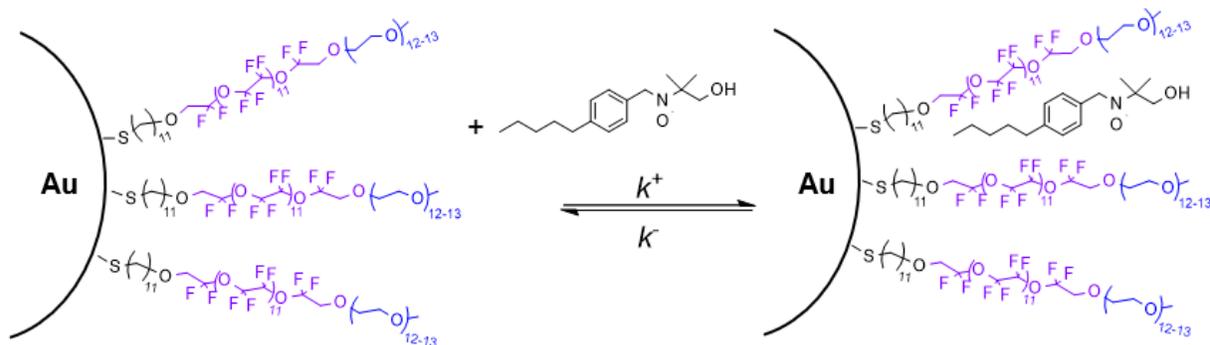


Figure 1. Graphical representation of a radical probe hosted in the AuNPs monolayer, in equilibrium with the free probe.

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Visible light effects on photostrictive/magnetostrictive PMN-PT/Ni multiferroic heterostructure

Deepak Dagur,^{*1,2} Vincent Polewczyk,² Aleksandr Yu. Petrov,² Pietro Carrara,^{2,3} Marta Brioschi,^{2,3} Sara Fiori,² Riccardo Cucini,² Giorgio Rossi,^{2,3} Giancarlo Panaccione,² Piero Torelli,² and Giovanni Vinai²

*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

Tuning the interfacial properties of a multiferroic heterostructure via fully optical means, specifically by exploiting the photovoltaic/photostrictive effect of its ferroelectric component, is a reversible and fatigueless method for modifying the magnetic response of magnetostrictive ferromagnets¹⁻³. In this study, we present the effects of 405 nm visible-light illumination on both the ferroelectric and ferromagnetic responses of (001) PMN-PT/Ni heterostructure.

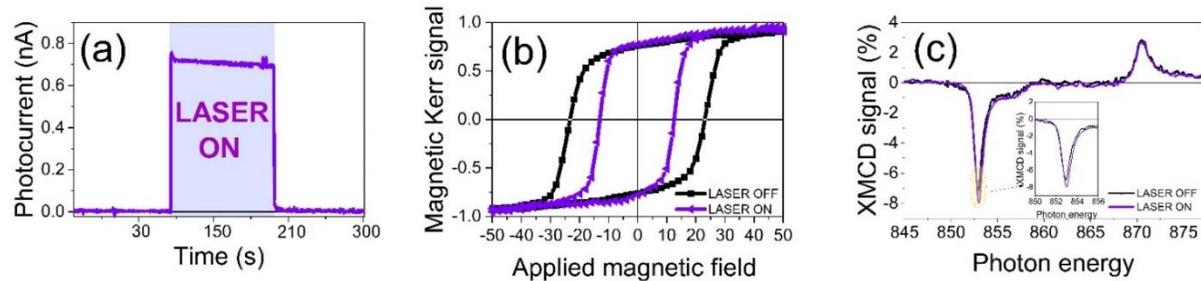


Figure 1. (a) Photocurrent measurement, (b) magnetic hysteresis loop and (c) XMCD spectra at Ni L_{2,3} edges of PMN-PT/Ni heterostructure with and without 405 nm light illumination.

By combining electrical, structural, magnetic and spectroscopic measurements, we show that light illumination above the ferroelectric bandgap energy induces a photovoltaic current (see fig. 1a), while the triggered photostrictive effect in PMN-PT induces a reduction of the coercive field of the interfacial magnetostrictive Ni layer (see fig. 1b). We firstly report a light-induced variation in the Ni orbital magnetic moment, direct signature of the photostrictive effects on Ni, obtained via sum-rule analysis of x-ray magnetic circular dichroic (XMCD) measurements (see fig. 1c). The observed effects are maximized when PMN-PT presents both in-plane and out-of-plane ferroelectric domains, and are strongly reduced once polarized out-of-plane, proving the central role played by in-plane ferroelectric domains⁴.

These results shed light on the delicate energy balance that leads to sizeable light-induced effects in multiferroic heterostructures, confirming the need of spectroscopy for identifying the physical origin of interfacial phenomena.

Acknowledgements: Nanoscience Foundry and Fine Analysis (NFFA-MUR Italy Progetti Internazionali) project.

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Imaging and characterization of fibrotic tissues

Lorenzo D'Amico,^{1,2,*} Giuliana Tromba,² Christian Dullin,³ Giovanni Birarda², Heinz Amenitsch,⁴ and Loredana Casalis²

*lorenzo.damico@elettra.eu

¹ Department of Engineering and Architecture, University of Trieste, via Valerio 64, 34127 Trieste, Italy

² ELETTRA Sincrotrone Trieste S.C.p.A Basovizza, S.S. 14, km 163,5 in Area Science Park, 34149 Basovizza (Trieste), Italy

³ Institute of Diagnostic and Interventional Radiology, University Medical Center Goettingen, Robert Koch Strasse 40, Goettingen, Lower Saxony 37075, Germany

⁴ Institute of Biophysics and Nanosystems Research, Austrian Academy of Sciences, Schmiedlstraße 6, 8042, Graz, Austria

Fibrosis is a general term for diseases that lead to an increased deposition of fibers, independent by potentially different underlying pathomechanism. Fibrosis is might turn into a life threatening condition as it can change the mechanical properties of the organs involved, i.e., stiffness and compliance. In this work we aim to characterize lung fibrosis. The lung architecture is comprised by a complex combination of several different fiber types, such as collagen, elastin, and fibrin. Unfortunately, little is known about the underlying pathomechanisms in lung fibrosis and if there are different subtypes, which in turn hinders the development of therapies. Thus, the first step would be to identify different subtypes of lung fibrosis by analyzing in detail fiber types, fiber concentration and orientation. Therefore, the aim of this project is to exploit different techniques to gain as many information as possible and contribute to shed some light on this disease when it occurs in the lungs. A combination of different imaging techniques was impossible so far as they require different sample preparation. Another aspect that hinders the analysis is the fact that lung fibrosis does typically not occur homogenously (figure 1) in the organ, so getting the same relevant regions analyzed by each technique was challenging.

In this work we decided to combine the following techniques: i) Synchrotron radiation computed microtomography (SR micro-CT) – to study the 3D anatomical structure and to guide the other techniques to fibrotic regions, ii) Fourier Transform Infrared Spectroscopy (FTIR) to analyze the chemical compositions of the fibrotic regions, iii) Small angle X-rays Scattering (SAXS) to quantify difference in the fiber orientation, iv) Atomic Force Microscopy (AFM) to get an estimate on alterations of the mechanical properties of the tissue, v) Soft X-ray Fluorescence (XRF) as a second technique to get a chemical fingerprint of the fibrotic regions and vi) Particle-Inducted X-Ray Emission (PIXE)

In order to establish this multimodal approach, we used two well characterized mouse models for lung fibrosis a) bleomycin induced fibrosis and b) genetically induced lung fibrosis. To validate the results classical histology was performed as well.

So far, we have performed a porosity analysis of the 3D reconstructions acquired with the SR micro-CT to characterize the tissue morphology. We extract 6 cubes per region, for a total of 3 regions per sample. We evaluate the amount of tissue vs. the quantity of air and we find out that there is a correlation between the tissue volume and the level of fibrosis, i.e., high values of tissue volume correspond to fibrotic regions whereas low values of tissue volume correspond to healthy region. Then a chemical analysis by means of the FTIR to gain information about the collagen content in the lung and subsequently the biomechanical properties of the same portion of tissue were measured with the AFM. For the other techniques the data analysis is still in progress. What we would like to establish using SAXS

is if there are different patterns in the fiber orientation whereas with XRF and PIXE we get an element map of the tissue.

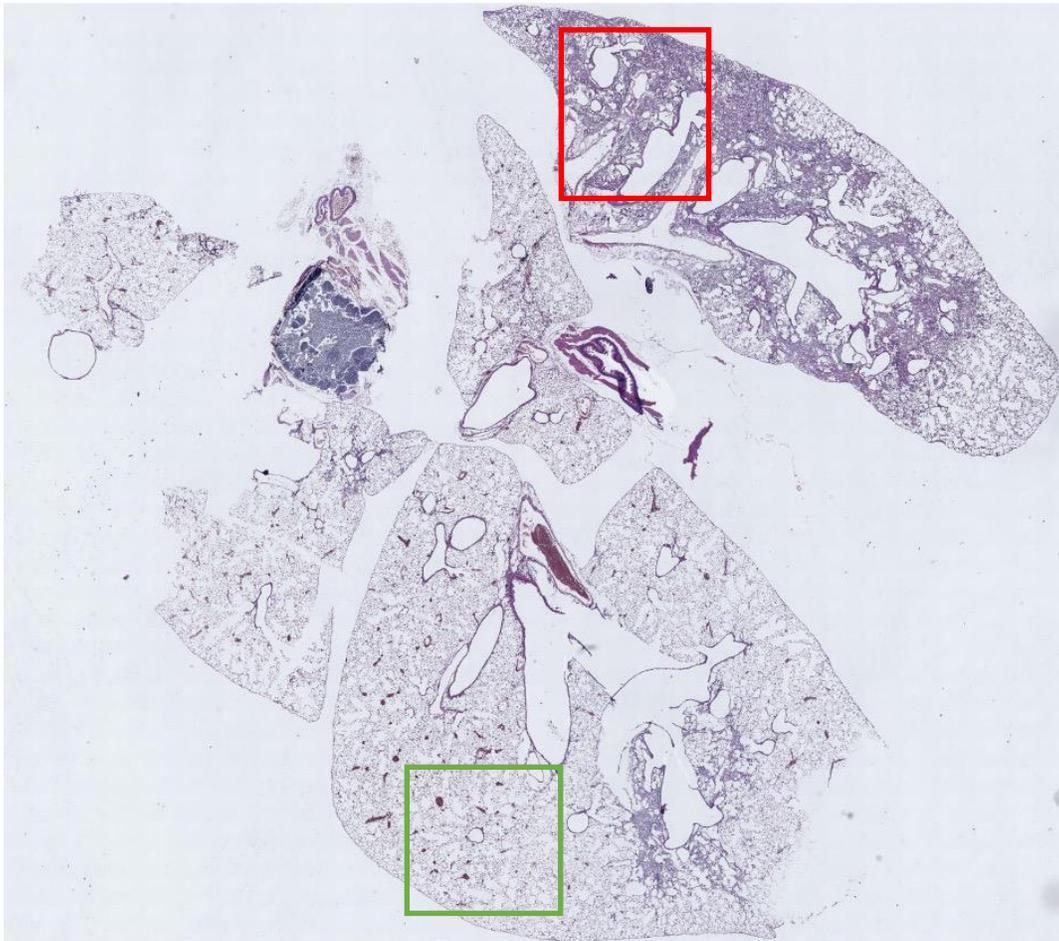


Figure 1. Example of the inhomogeneity of fibrosis.

Mechanical systems for the understanding of cellular mechano-response at the nanoscale

Giorgia Demontis,^{1,2*} Martina Conti,² Ilenia Virgili,³ Marco Lazzarino,² Paul Heppenstall,⁴ and Laura Andolfi²

* GIORGIA.DEMONTIS@studenti.units.it

¹University of Trieste, Department of Physics, 34100 Trieste, Italy

²CNR-IOM, SS 14 km 163,5 Area Science Park Basovizza, 34149 Trieste, Italy

³University of Trieste, Department of Life Sciences, 34100 Trieste, Italy

⁴SISSA: Scuola Internazionale Superiore di Studi Avanzati, Via Bonomea, 265, 34136 Trieste, Italy

Living cells within a tissue are constantly exposed to mechanical stimuli arising from the surrounding extracellular matrix or from neighboring cells. The molecular processes through which such mechanical cues are converted into a biological response are called mechanotransduction events. This process is activated and regulated by several cellular elements: the cell membrane (1), the cytoskeleton (2), proteins of focal adhesion sites and mechanically gated ion channels (3). Among them, mechanosensitive channels Piezo 1 and 2 have been identified as relevant functional elements of the mechanotransduction machinery (4). Piezo1 has been found to be expressed in different kind of cells (e.g. red blood cells, lungs, bladder, pancreas, and uterine endometrium), while Piezo 2 is mostly expressed in dorsal root ganglia neurons (5), lung, gastrointestinal tract, and skin. This latter channel is particularly important in the somatosensory system. In vivo Piezo channels are located at the periphery of the DRG neurons, while DRG in culture lose this polarization and Piezo channels are observed evenly distributed on the cell surface.

In order to investigate how a specific mechanical stimulus can affect the activity of Piezo channels and whether such stimulus can induce a specific membrane relocation of the channels we intend to use different approaches to apply well-defined mechanical stimulus to cells in terms of intensity and direction. In this work we used a breast cancer cell line (MDA-MB-231) expressing Piezo channels, as cellular model to test the effect of different mechanical stimulus on the activity of these channels. Specifically, these cells were cultured on substrates with different stiffness or on stretchable membranes to deliver to the cells both a static or an active mechanical cue. In both cases, after 24h culturing, the activity of the calcium permeable mechanosensitive channels was monitored by calcium imaging.

This study will pave the way to the development of a support able to integrate different mechanical stimuli, for investigating whether and how a well-defined mechanical stimulus act on Piezo 2 channel activity and its distribution in DRG.

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

Ayesha Farooq,^{1,2,3} Matus Stredansky,³ Simone Dal Zilio,³ and Cinzia Cepek³

*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, Strada Statale 14, Km.163.5 I-34149 Trieste, Italy

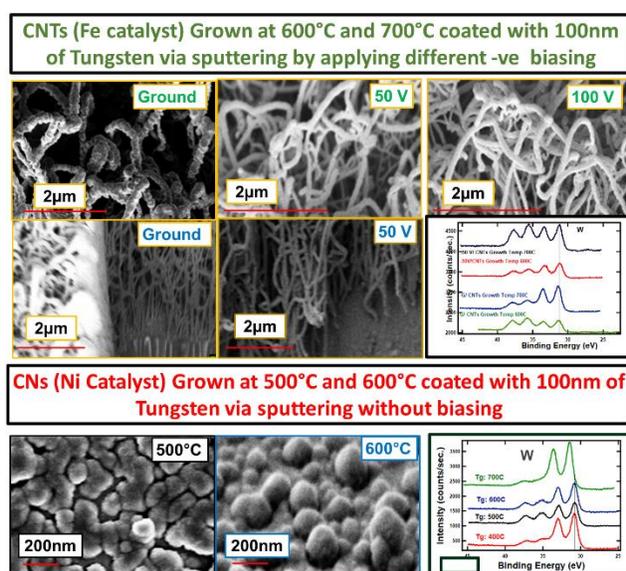
Hybrid materials have the potential to replace traditional materials. They show improved mechanical and physical properties, there are many applications in which hybrid materials are used such as coating, nanocomposite, medical [1], optical, energy storage [2], fusion energy [3], and gas sensing [4].

The first wall experiences, high heat loads, thermal shocks, the bombardment of neutrons, and tritium retention. This Ph.D. project aims at the synthesis and study of carbon nanotubes and tungsten hybrid nanomaterials of controlled and reproducible size and morphology for applications in fusion reactors [5]. We have grown different carbon nanostructures (CNs) on Silicon/SiO₂ and Si/Al₂O₃ wafers via chemical vapor deposition (CVD) using Fe and Ni as catalysts. The obtained CNs are coated with tungsten films 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 techniques, including X-ray photoemission spectroscopy (XPS), Raman, XRD, AFM, and scanning electron microscopy (SEM), allowing us to understand how the different process parameters influence the final properties of the synthesized films, e.g., their morphology, stoichiometry, and electronic properties.

CNTs are used as a template to deposit W. By changing the deposition parameters for W the crystallinity, morphology, and stoichiometry of the sample changes.

Acknowledgments: ENI for funding the project.

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Insights into the behavior of cholesterol in the modulation of lipid rafts derived from model membrane systems: their interactions with differently functionalized gold nanoparticles

Elena Ferraguzzi,^{1,2*} Carolina Paba,^{1,2} Behnaz Abbasgholi-Na,² Pietro Parisse,³ and Loredana Casalis²

*elena.ferraguzzi@phd.units.it

¹ Department of Physics, University of Trieste, 34127 Trieste, Italy

² Elettra-Sincrotrone Trieste S.C.p.A SS 14 Km 163.5 in Area Science Park 34149 Basovizza, Trieste, Italy

³ Istituto Officina dei Materiali – CNR s.s 14 km 163.5 in Area Science Park 34149 Basovizza- Trieste-Italy

Model systems of eukaryotic cellular membranes as supported lipid bilayers (SLBs) are employed here to elucidate the lateral mixing of lipids at the cellular interface as well as their interactions with different molecular players¹. Our model system consists of 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC), 1,2-distearoyl-sn-glycero-3-phosphocholine (DSPC), Sphingomyelin (Brain, Porcine, SM) at stoichiometric ratio of (35:20:12), at different cholesterol concentrations, namely $\chi=0.05, 0.25$ and 0.33 , for mimicking an idealized eukaryotic cellular membrane bearing a certain degree of complexity. These lipids in fact phase-separate forming ordered phases, transient membrane subdomains called lipid rafts, embedded in gel-like phases. The role of cholesterol in the modulation of lipid rafts order, which is known to be involved in the regulation of cellular activity², has been investigated through atomic force microscopy (AFM) topographic measurements in physiological environment. We observed that raft domain height decreases as cholesterol concentration increases, while the lateral dimension of lipid rafts increases in size. Then, we studied the interaction between SLBs and AuNPs functionalized upon formation of self-assembled monolayers of TOEG6 (Toeg6@AuNPs) and mixed monolayer of TOEG6 and short ssDNA oligos (22 bases, Toeg6-ssDNA@AuNPs)³ respectively, to understand the role of membrane rafts in modulating the interaction. Our measurements show that Toeg6-ssDNA@AuNPs can internalize in the rafts more than Toeg6@AuNPs. To get more insights on the interaction, we produced liposomes at an equivalent relative lipid concentration of SLBs. Through UV-Vis spectroscopy measurements then we monitored the UV-VIS absorption changes related to the variation of surface plasmon resonance (SPR) of AuNPs in interaction with the liposomes. According with literature,⁴ SPR of citrate@AuNPs adsorbed on liposomes is sensitive to the liposome's mechanical properties. The aggregation of citrate@AuNPs is promoted by fluid-phase membranes and this effect results in an absorption change from 590 to 620nm. Our results show that the aggregation is promoted as the cholesterol concentration increases, indicating that liposomes composed of $\chi=0.33$ are the softest ones. We then investigated the interactions between liposomes and functionalized gold nanoparticles. We found a broadening of the SPR band for both Toeg6@AuNPs and Toeg6-ssDNA@AuNPs, and therefore high particle aggregation level, when they are incubated with $\chi=0.33$ cholesterol liposomes. No shift/broadening is present in the case of $\chi=0.05$ chol. liposomes. Our findings indicate that Toeg6-ssDNA@AuNPs may represents a great potential player in the modulation of membrane activity, and an interesting platforms for further biophysical applications.

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Computational insight into hydrogen evolution reaction on Pt surfaces

Lea Gašparič^{1,2,*} and Anton Kokalj^{1,2}

*lea.gasparic@ijs.si

¹ Department of Physical and Organic Chemistry, Jožef Stefan Institute, Ljubljana, Slovenia

² Jožef Stefan International Postgraduate School, Ljubljana, Slovenia

Platinum is the most efficient electrocatalyst for hydrogen evolution reaction (HER) requiring only a minimal overpotential in acidic media. Understanding the surface chemistry of Pt could facilitate the development of new highly efficient electrocatalysts. Calculations based on density functional theory (DFT) have proven valuable for thermodynamic and kinetic analysis of various catalytic reactions. For the study of electrocatalytic reactions, excess charges and electrode potential must also be considered. The simplest method that can be applied to HER within DFT framework is computational hydrogen electrode¹, which was also used for this study.

We analyzed the reactivity of Pt(111) and Pt(100) surfaces for HER. Thermodynamic stability of various adsorbed H and OH structures at different pH and electrode potentials was calculated on the two surfaces. Pt(100) is more reactive and exhibits higher coverage of adsorbates than Pt(111). The latter can exist free of investigated adsorbates in a wide range of pH values and electrode potentials. Analysis of surface reaction free energies at pH=0 reveals the adsorption of proton as the most exothermic step, while the formation of hydrogen molecule is endothermic on both surfaces.

Calculations of transition states for the Tafel step ($H_{(ads)} + H_{(ads)} \rightarrow H_2$) were conducted in vacuum on Pt(111) and Pt(100) surfaces for different coverages of $H_{(ads)}$. Activation and reaction energies decrease with increasing coverage on both surfaces, but for the same coverage, Pt(111) gives lower energy barriers than Pt(100). All three elementary steps of HER (Volmer, Tafel, and Heyrovsky) were studied with ice-like layer of water molecules on Pt(111). Volmer step ($H^+ + e^- \rightarrow H_{(ads)}$) has the lowest activation energies and Heyrovsky ($H^+ + e^- + H_{(ads)} \rightarrow H_2$) the highest. This indicates that HER on Pt goes through Volmer–Tafel mechanism with the Tafel step being rate determining.

Acknowledgements: The authors would like to acknowledge the collaboration with the Laboratory for Electrocatalysis from the National Institute of Chemistry, Slovenia. This work has been supported by the Slovenian Research Agency (Grant no. PR-11454).

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Optimization of in-situ growth of Al/InAs hybrid systems on GaAs for the development of Andreev qubits title

M. Kirti,^{1,2*} M. Sütő,³ E. Tóvári,³ P. Makk,³ T. Prok,³ S. Csonka,³ P. Banerjee,² P. Rajak,² R. Ciancio,² J. R. Plaisier,⁴ and G. Biasiol²

* magdhi.kirti@phd.units.it

¹ Department of Physics, University of Trieste, 34128 Trieste, Italy

² IOM CNR, Laboratorio TASC, Area Science Park Basovizza, 34149 Trieste, Italy

³ Department of Physics, Budapest University of Technology and Economics and Nanoelectronics "Momentum" Research Group of the Hungarian Academy of Sciences, 1111 Budapest, Hungary

⁴ Elettra-Sincrotrone Trieste S.C.p.A., Area Science Park Basovizza, 34149 Trieste, Italy

Two-dimensional electron systems confined near the surface of narrowband semiconductors have piqued interest due to their ease of integration with superconductors, 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 most promising candidates, as high-quality superconducting thin films with transparent interfaces to a low-D semiconductor will improve coherence time as well as offers strong qubit-qubit coupling [1]. 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 [2,3].

In this work we have demonstrated that in-situ growth of aluminium films on near-surface InAs 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 [4]. 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 (Figure 1). The growth protocol developed could thus set a new standard for the fabrication of Andreev qubits on GaAs technology.

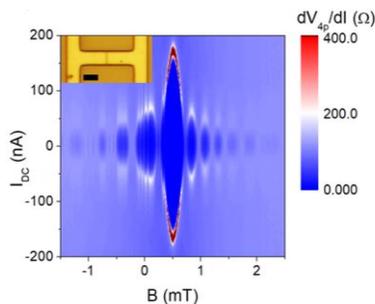


Figure 1. Shows the Fraunhofer pattern in the differential resistance of Josephson junction.

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Core level anomaly in oxidized size-selected Ag_n clusters on graphene

Federico Loi,¹ Monica Pozzo,² Luca Sbuelz,¹ Luca Bignardi,¹ Paolo Lacovig,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 Dipartimento di Fisica Ettore Pancini, Università di Napoli Federico II, Monte S. Angelo, I-80126 Napoli, Italy

Supported size-selected clusters have emerged in the past decades for their unique features, which are often very different from their bulk analogues.¹ In this talk, I will discuss how we studied the oxidation of size-selected Ag_n clusters ($n = 7$ and 11) supported on graphene by means of experimental and theoretical X-ray photoelectron spectroscopy (XPS). XPS is a powerful technique to fingerprint the oxidation state of an atom thanks to the correlation between this value and energy of the core level lines.² However, our results indicate that in the case of size selected Ag_n clusters, this correlation breaks down. While in the case of oxidized surfaces and thin films the Ag 3d core level binding energies progress linearly as $\text{Ag}(0) > \text{Ag}(I) > \text{Ag}(III)$,³ in the clusters the binding energy for Ag(III) is larger than for Ag(I). We investigated this anomaly by means of DFT calculations to find out that it is related to a unique behavior of the center of the Ag 4d-band for increasing O coverages. This parameter, which is a well-known indicator of chemical reactivity,⁴ is almost unaffected by oxidation at larger scales, while it drastically changes in the clusters. This effect propagates to the core level binding energies, causing the anomaly that we observed. Our result highlights the unique properties of size-selected clusters with respect to their counterparts at larger scales and links the measured core level shifts to an enhanced reactivity of the oxidized Ag_n clusters.

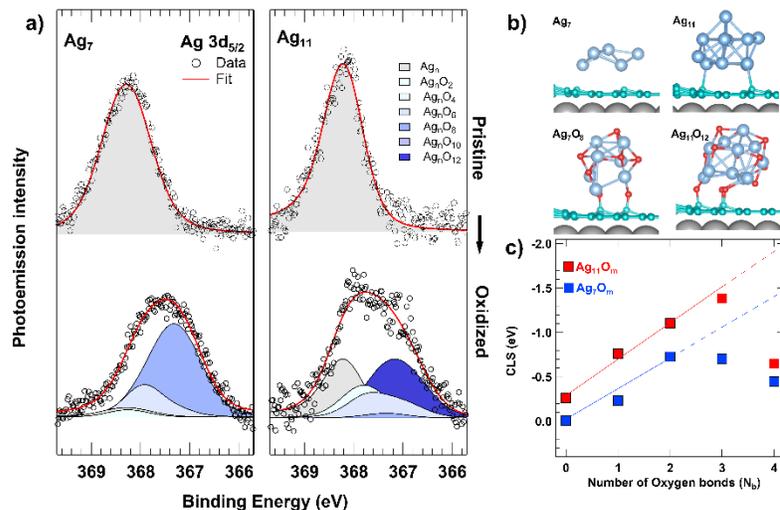


Figure 1. a) Experimental XPS spectra and b) DFT calculated geometries of pristine and oxidized Ag_n clusters ($n = 7$ and 11) supported on graphene epitaxially grown on Ru(0001). c) Trend of the average Ag 3d_{5/2} core level shift of the atoms in the clusters as a function of the number of oxygen bonds.

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Bismuth-based electrocatalysts for CO₂ conversion towards value-added products

Miriam Marchi,¹ Michele Cacioppo,² Michele Melchionna,^{1,*} and Paolo Fornasiero^{1,*}

*melchionnam@units.it, pfornasiero@units.it

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

² CIC biomAGUNE, Paseo de Miramón 182, 20009 Donostia, San Sebastián, Spain

Among the various approaches for CO₂ mitigation, the electrocatalytic CO₂ reduction represents an appealing strategy incorporating to the circular economy concept. CO₂ conversion can lead to a variety of possible compounds, such as carbon monoxide, methane, formic acid, methanol, ethylene.⁽¹⁾ Formic acid (FA) is an attractive product, considering its application as hydrogen storage vector and its use for direct formic acid fuel cells. In recent years, bismuth-based materials have been identified as excellent electrocatalysts for the formation of FA as the main product of CO₂ hydrogenation.^(2,3)

We investigated the properties of hybrid catalysts based on bismuth oxide (Bi₂O₃) supported on carbon nanostructures (CNSs) to produce FA by electrocatalytic CO₂ conversion.⁽⁴⁾ The merging of an inorganic component with a carbon nanostructure has been proven to enhance the electrical conductivity and to improve the dispersion and structural stability of the inorganic material.⁽⁵⁾ Specifically, we focused on the use of single-walled carbon nanohorns (SWCNHs), which offer some advantages such as a higher surface area as compared to graphene (G) or carbon nanotubes (CNTs). Moreover, they are synthesized by procedures not involving use of metal catalysts, so that no metal impurities remain attached. The employment of CNHs in the preparation of Bi₂O₃ nanoparticles leads to the formation of organic-inorganic interfaces, which are fundamental in tuning the catalytic properties of nanomaterials. We extensively tested Bi₂O₃-CNHs hybrids for CO₂ electro-reduction in aqueous electrolyte, yielding formic acid with high selectivity and low overpotentials.

To move beyond the formation of formic acid and to range in different value-added compounds, we aimed to perform CO₂ reduction simultaneously coupled with esterification of FA with ethanol, through an acid catalyzed reaction. This new approach allows to obtain ethyl formate (EF), a chemical with applications ranging from solvent use to pharmaceutical intermediates, insecticide, flavors and others. However, the two steps involved in the formation of the target carbon product (1. CO₂ reduction reaction towards formic acid and 2. esterification process) usually require different conditions for achieving sufficient performances. For this reason, we identified that in-depth study of catalytic conditions and design of bi-functional catalysts are the key steps for a successful production of EF. We evaluated the role of the electrolyte, and we developed different catalysts for the two stages involved. In particular, we introduced acidic sites on SWCNHs by sulfonation process, obtaining a heterogeneous acid catalyst for the esterification step. This work represents the first effort in order to directly produce EF by converting CO₂.

Acknowledgements: This work was supported by the University of Trieste, INSTM and the European Commission (DECADE).

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AuNPs green synthesis: the effect of natural compounds

Caterina Medeot,^{1,2,*} Ahmed Alsadig,^{2,3} Francesco D'Amico,⁴ Albano Cossaro,^{4,5,6} Hendrik Vondracek,^{2,4,7}
Giovanni Birarda,⁴ Paola Posocco,⁸ Pietro Parisse,^{2,5} Loredana Casalis,² and Serena Bonin¹

*caterina.medeot@phd.units.it

¹DSM – Department of Medical Sciences, University of Trieste, 34149 Trieste, Italy

²NanoInnovation Lab, Elettra Sincrotrone Trieste S.C.p.A., 34149 Trieste, Italy

³Institute of Nanotechnology – National Research Council (CNR-NANOTECH), Campus Ekotecne, 73100 Lecce, Italy

⁴Elettra-Sincrotrone Trieste S.C.p.A., Area Science Park, 34149 Trieste

⁵Istituto Officina dei Materiali - National Research Council (CNR-IOM), Area Science Park, 34149 Trieste, Italy

⁶Department of Chemical and Pharmaceutical Sciences, University of Trieste, Trieste, 34127, Italy

⁷Diamond Light Source Ltd, Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0DE, UK

⁸Department of Engineering and Architecture, University of Trieste, 34127 Trieste, Italy

During last decades metal nanoparticles gained enormous scientific and technological interest, as drug delivery systems or biosensors¹. Gold nanoparticles (AuNPs) are the most used for their stability, low toxicity, chemical inertness, and biocompatibility². They are routinely synthesized by reduction of a precursor with chemical reagents, which produce toxic wastes in organic solvents³. This research focused mainly on green chemistry approach, with the aim of minimizing chemical wastes and production costs. AuNPs biosynthesis can be achieved with plant tissues⁴, microorganisms⁵, or other biological sources. Unfortunately, current studies lack of standardized synthesis procedures. Likewise, the nature of the reducing agent that drives the nanoparticles formation is still unclear. The present work aims at comparing AuNPs synthesis procedures obtained using different natural extracts with the purpose of finding the most efficient and environmental-friendly one. A careful spectroscopic and morphological analysis has been applied to infer the nature of the redox reaction driving the AuNPs formation and to identify the best protocol that could be adopted to generate small, clean, spherical and monodisperse AuNPs. Spherical AuNPs were successfully synthesized from cocoa extract with a size distribution of 10-11 nm. Spectroscopic analyses revealed the presence of fatty acids, protein residuals and flavonoids, especially catechin, in cocoa extracts and AuNPs. Furthermore, selected AuNPs obtained from cocoa extracts were deeply characterized and then functionalized with single-stranded DNA (ssDNA) fragments, which in turn can be potentially used in drug delivery and biosensing.

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Carbon nanotubes-based biosensor as a tool for sensing of Dopamine

Giuseppe Misia,¹ Alessandro Silvestri,² and Maurizio Prato^{1,2,3}

giuseppe.misia@phd.units.it

¹ Department of Chemical and Pharmaceutical Sciences INSTM Udr Trieste, University of Trieste via Licio Giorgieri 1, 34127 Trieste, Italy

² Center for Cooperative Research in Biomaterials (CIC biomaGUNE), Basque Research and Technology Alliance (BRTA), Donostia-San Sebastián, 20014 Spain

³ Ikerbasque, Basque Foundation for Science, 48013 Bilbao, Spain

The implementation of 1D and 2D nanomaterials in sensing technology has greatly improved sensitivity, linear range and stability of biosensors, especially for electrochemical sensing, thanks to their outstanding electronic properties.^{1,2} The aim of this project is to further explore the applicability of materials like Carbon Nanotubes, Graphene and Molybdenum Disulfide for electrochemical sensing, by bringing forward the current state of art about their synthesis and functionalization.³⁻⁵

Here we show you some of the first results obtained with our first material, Multiwalled Carbon Nanotubes (MWCNT) functionalized with Metal Vapor Synthesized (MVS) Au Nanoparticles, for electrochemical sensing of bioreceptors, like L-Dopamine and epinephrine.

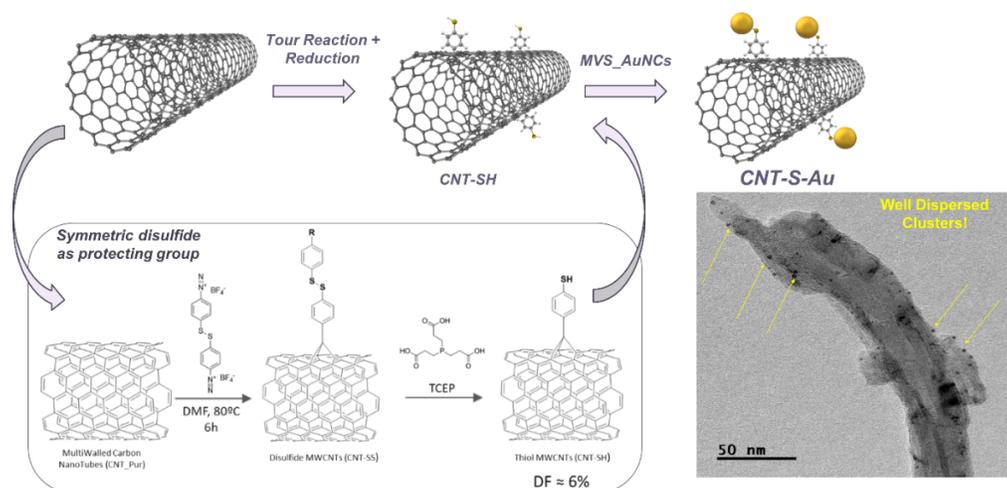


Figure 1. Design of the material and TEM image of CNT-Au hybrid material.

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Soft x-ray absorption spectroscopies of CuNPs in liquids

Ilargi Napal Azcona,^{1,*} Silvia Nappini,² and Elena Magnano,²

*ilargi.napalazcona@phd.units.it

¹ Università degli Studi di Trieste, Physics Department, P.le Europa 1, 34127 Trieste, Italy

² IOM-CNR, Istituto Officina dei Materiali, AREA Science Park Basovizza, 34149 Trieste, Italy

The need to understand and control the dynamics of electronic properties at the solid/liquid or solid/gas interface during physical and chemical reactions is fundamental for the optimization of catalytic materials. Thus, there is a growing demand for in situ and real working conditions (*in operando*) analysis. Spectroscopic techniques based on synchrotron radiation like X-ray absorption (XAS) can provide important information about reactions that involve the transfer of one or more electrons. Moreover, the energy of photons and electrons emitted during these reactions can give us information about the interactions with the surroundings and the chemical state of the elements of interest.

The last approach developed at BACH beamline in collaboration with the IOM-CNR to adapt XAS to *in operando* conditions is based on the use of an electrochemical cell equipped with microfluidic channels, provided with X-ray transparent Si₃N₄ window (Fig.1) (1).

Copper nanoparticles (Cu NPs) are of interest as catalysts for a broad range of applications like industrial processes, electronics, sensors or biomedical applications (2). Copper oxide catalysts have shown enhanced activity for different reactions, and it is well established that their selectivity is dependent on the oxidation state and the structural morphology (3).

By using *in situ* soft XAS, we tracked the oxidation and reduction of electrochemically deposited CuNPs while different potentials were applied. In parallel, scanning electron microscopy (SEM) characterization was performed to correlate the copper oxidation state with the morphology of the nanoparticles.

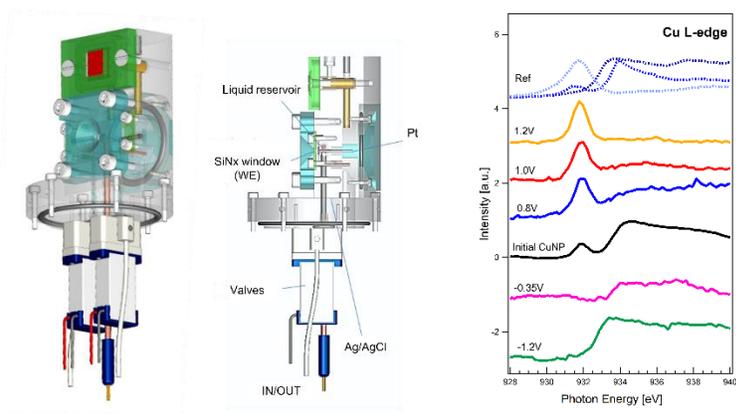


Figure 1. Schematic drawings of the microfluidic electrochemical cell developed at BACH beamline (left). *In operando* Cu L-edge XAS measurements of CuNPs at different applied potentials.

Acknowledgements: Federica Bondino and Igor Piš.

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Biophysical study on small extracellular vesicles (sEVs) interaction with model plasma membrane

C. Paba,^{1,5} B. Senigaglia,² N. Tormena,³ P. Parisse,^{4,5} K. Voitchovsky,³ and L. Casalis^{1,5,*}

[*loredana.casalis@elettra.eu](mailto:loredana.casalis@elettra.eu)

¹University of Trieste, Trieste, Italy

²IINS, Bordeaux, France

³University of Durham, Durham, United Kingdom

⁴IOM-CNR, Trieste, Italy

⁵Elettra Sincrotrone Trieste, Trieste, Italy

Small extracellular vesicles (sEVs) represent nowadays the most promising communication route between distant cells for delivering biological information throughout the body. They are indeed released by almost all types of cells, displaying a nanometer size (30-300 nm), and a molecular composition enriched with endosome-derived components. By traveling in bodily fluids (e.g. blood, saliva), they can cross biological barriers escaping the immune response, strongly impacting the fate of recipient cells. However, a deep knowledge of the mechanisms regulating the selective release and uptake by cells in our body is still missing, and crucial to repurpose EVs for therapeutic usage. Nevertheless, the surface pattern of both the EVs and the recipient cell and the ability of lipids to fuse plays an important part. To that end, using artificial model membranes for studying such biological processes, represents an innovative strategy for understanding, with a high temporal and spatial resolution, the molecular aspects involved in EVs' uptake and internalization pathways.

With the present work, we here propose a time and resolution-resolved approach based on Atomic Force Microscopy study on a supported lipid bilayer to mimic the interplay between EVs and cell membranes. The interaction study, performed with small EVs isolated from a breast cancer cell line, highlighted their ability to fuse with the supported lipid bilayer when the latter is textured with liquid-ordered and liquid-disordered domains enriched with cholesterol. Moreover, once the fusion process starts, the degree of order of the model membrane decreases, with the fluidification of the liquid-ordered phase as a consequence. Furthermore, while analysing the interplay between EV and model membranes in the absence of cholesterol, a preferential EV interaction with the solid-ordered phase is observed, regardless of the chemical composition of such domains. These results suggest two main important features in the EV interaction process: the first one is that EV uptake is not primarily modulated by the cholesterol percentage but it is governed by the fluidity of the proposed model; the second one is that the process is based on a physical interaction among the two systems, which in turn is maximized for the model without cholesterol, even though it requires a non-zero cholesterol concentration for the process to spread. Based on that, given the high demand and the wide use of EVs in biological sciences and nanotechnologies, we expect that our results will be useful for the selection of the crucial molecular aspects involved in EVs' selective uptake and internalization pathways by recipient cell membranes.

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Computational modelling of CeO₂-CuO catalyst for methane activation and functionalization

Carlo Federico Pauletti

Department of Physics, University of Trieste, via Valerio 2, 34127 Trieste, Italy

Ceria/copper interfaces are of particular interest thanks to their unique capacity to activate small molecules, making them good candidates as catalysts in a broad variety of processes¹. Among those, the activation of methane is particularly appealing due to its high abundance and availability, making it both an attractive energy source and a widely employed building block for the production of a great variety of fine chemicals². Unfortunately, methane functionalization is often hard to achieve as it requires cleavage of the highly energetic C-H bond (440 kJ/mol).

Recently, the research group led by Prof. Trovarelli at the University of Udine prepared a ceria-copper oxide mixed catalyst capable of activating the C-H bond of methane at relatively low temperature. They employed ball-milling, a cheap and simple synthetic procedure which involves mixing and sintering of powders thanks to the mechanical energy provided by hard spheres.

Operando NEXAFS measurements performed on catalysts activated at 300°C show evidence of a charge transfer occurring between the Ce³⁺/Cu²⁺ redox couple, which is not present in similar samples prepared through impregnation. Moreover, in contrast to the behavior of impregnated samples and to pure CuO and CeO₂, methane activation on the ball milled samples occurs at the relatively low temperature of 250°C, as evidenced by the presence of methoxy C-H stretching bands in the IR spectra collected upon methane exposure.

We employed computational tools to elucidate such experimental results, with the main goal of finding a plausible correlation between the electronic structure of the catalyst and its catalytic properties. Ab-initio DFT calculations support the experimental evidence of a charge transfer occurring between Ce³⁺ and Cu²⁺ upon interfacing, and methane activation through C-H bond cleavage at the interface is considerably facilitated compared to the two isolated parent oxides, in agreement with experimental results. Moreover, we found that oxygen vacancies are easily created on the mixed catalyst in comparison to the two isolated oxides. We also determined that a number of special adsorption sites is generated upon interfacing the two lattices, on which methane adsorption is particularly favorable thanks to a variety of contributing factors.

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Seaweed polysaccharides for novel applications and products

Francesco Piazza,^{1*} Pasquale Sacco,¹ and Ivan Donati¹

*francesco.piazza2@phd.units.it

¹ Department of Life Sciences, University of Trieste, Via L. Giorgieri 5, 34127 Trieste, Italy

Extracellular matrix (ECM) owns complex mechanical milieu characterized by non-linear, plastic, and viscoelastic behaviour. Cells are able to perceive this biophysical milieu and convert the resulting external mechanical forces into intracellular biochemical signals through a process called mechanotransduction^{1,2}. Stiffness and viscoelasticity (in terms of stress relaxation or loss tangent) are the mechanical feature that play a key role in the mechanosensing process of the cell^{3,4}. Recently, a novel property has been shown to steer cell behaviour, namely the energy associated with the linear stress-strain response of materials under oscillatory shear^{5,6}. This elastic energy represents the energy required to enter into the non-linear (plastic) region.

In this project, our interest focused on the development of viscoelastic agarose-based hydrogels with tunable mechanical characteristics, especially elastic energy, to use as ECM-like substrates to investigate cell mechanobiology. At first, different systems with varying chemical compositions and polymer concentrations were studied mechanically by rheometry and biologically by cell adhesion test. Results defined the hydrogels as fast relaxing materials with a shear modulus that increase with polymer concentration and an elastic energy inversely proportional to the percentage of polymer content. The number of adherent cells decreased with increasing elastic energy. Taken together, these data allowed us to identify a threshold value for energy above which cell adhesion is impaired. Below this threshold, cell growth is promoted at low energy regime where it is easier to break and remodel the substrate. Another investigation focused on agarose hydrogels prepared at different temperatures to compare the surface mechanical properties of the substrate with the bulk ones. Bulk characteristics were studied by uniaxial compression and rheological tests, while the surface was analysed by AFM, SEM, confocal profilometry and contact angle test. Overall, it appears that curing temperature has a structural and mechanical impact on the surface properties of the matrix, while the effect on the bulk mechanical properties is related to the elastic energy alone.

Altogether, our work brought new knowledge about viscoelastic substrates to use as ECM-mimic models for mechanobiology studies. Furthermore, this finding confirms the importance of substrate elastic energy in the cell's decision-making process.

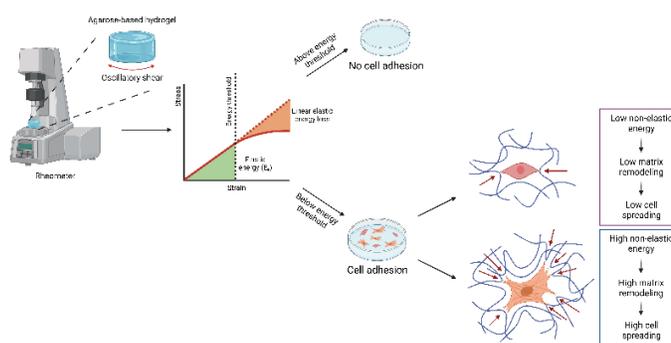


Figure 1. Schematic cartoon of the dependence of cell activity to elastic energy.

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Carbon vacancies steer the activity in dual Ni-carbon nitride photocatalysis

M. Marchi,¹ E. Raciti,^{1,2} S. M. Gali,² F. Piccirilli,³ H. Vondracek,³ A. Actis,⁴ E. Salvadori,⁴ C. Rosso,¹ A. Criado,⁵ C. D'Agostino,⁶ L. Forster,⁶ D. Lee,⁶ A. Foucher,⁷ D. Beljonne,² E. Stach,⁷ M. Chiesa,⁴ R. Lazzaroni,² G. Filippini,^{1,*} M. Prato,^{1,8,9} M. Melchionna,^{1,*} and P. Fornasiero^{1,*}

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

² Laboratory for Chemistry of Novel Materials, Materials Research Institute, University of Mons, Place du Parc 20, Mons 7000, Belgium

³ Elettra Sincrotrone Trieste, SS 163,4 km 14 in Area Science Park 34149 Basovizza, Trieste (Italy)

⁴ Department of Chemistry, University of Torino, NIS Centre of Excellence, Via Giuria 9, Torino 10125, Italy

⁵ Universidade da Coruña, Centro de Investigacións Científicas Avanzadas (CICA), Rúa As Carballeiras, 15071, A Coruña, Spain

⁶ Department of Chemical Engineering, The University of Manchester, Oxford Road, Manchester M13 9PL, UK

⁷ Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA-19104, USA

⁸ Center for Cooperative Research in Biomaterials (CIC biomaGUNE), Basque Research and Technology Alliance (BRTA), Paseo de Miramón 194, 20014, Donostia-San Sebastián, Spain

⁹ Ikerbasque, Basque Foundation for Science, Bilbao, Spain

Ni cross-coupling reactions are interesting and versatile processes by which new chemical bonds between convenient substrates can be formed^[1,2]. It is known that upon absorption of light, a convenient photocatalyst can initiate the reaction, for which Transition-Metal Photocatalysts (TMCs) were typically used in recent times^[3,4]. Despite their good performances, the environmental requirements are not met. Lately carbon nitrides have attracted considerable attention for being totally metal-free easily-synthesizable materials, which possess a low band-gap of about 2.7 eV^[5-7]. A particularly promising post-synthetic version, a microwave-treated carbon nitride (*mw-CN*), was prepared by us, showing a higher surface area and a higher number of superficial pores which can serve as potential binding sites. In presence of Ni(II) complexes, the material would coordinate them and facilitate the photoelectron-transfer.

In order to unravel the mechanism of such a difficult process, we employed Density Functional Theory with which we obtained the formation energies of hypothesized Ni(II) complexes coordinated to *mw-CN*, deducing their stability and finally we computed the electron-transfer at the excited states.

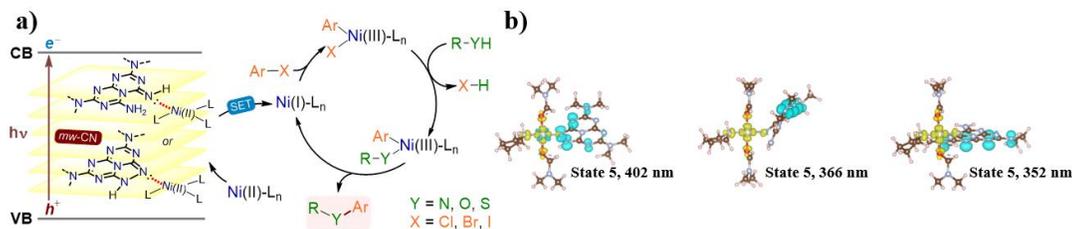


Figure 1: a) Microwave-treated carbon nitride coordinating Ni(II) complexes and scheme of the arylamination reaction; b) electron holes (h^+ , light-blue) and charges (e^- , yellow) of three selected computed transitions.

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Screen-printed graphite-based electrodes for electrochemical detection of Imidacloprid

Barbara Repič,^{1,2*} Maksimiljan Dekleva,³ Darko Belavič,¹ Kostja Makarovič, Mitja Jerlah,⁴ Ema Gričar,³
Helena Prosen,³ Mitja Kolar,³ Gregor Marolt,³ Danjela Kuščer^{1,2}

*barbara.repic@ijs.si

¹ Jožef Stefan Institute, Electronic Ceramics Department, Ljubljana, Slovenia

² Jožef Stefan International Postgraduate School, Ljubljana, Slovenia

³ Faculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia

⁴ CO NAMASTE, Ljubljana, Slovenia

Imidacloprid (IMD) is a synthetic pesticide used in agriculture that has harmful effects on the environment and human health. Since this compound has an electroactive nitro functional group, it can be detected by electrochemical (EC) techniques, which are a more practical and cost-effective solution than the conventional detection in laboratories using high-performance liquid chromatography coupled with tandem mass spectrometry (HPLC/MS-MS). Since the reduction of IMD occurs at fairly negative potentials, typically less than -1,0 V vs. Ag/AgCl, the generation of hydrogen at the working electrode (WE) can obscure the analytical signal, leading to some limitations in potentially suitable electrode materials. Carbon-based materials, such as graphite, glassy carbon, and various carbon nanostructures, have been most commonly studied for the detection of IMD¹⁻³. Our goal is to develop graphite-based thick films on an alumina substrate that can be used as WEs and would exhibit the EC response to IMD.

The paste, prepared by dispersing 15 vol% graphite powder in a terpineol-based vehicle, was screen printed in an 8 mm x 8 mm square shape on an alumina substrate. After annealing the graphite layer (GE) at 850°C in an argon atmosphere, it was about 30 μm thick, had a homogeneous surface and a sheet resistance of 7 Ω/sq, but poor adhesion to the substrate. To improve the adhesion, the graphite-glass composite (GGE) layers were prepared with different graphite:glass weight ratios. The results confirm that the glass improves the adhesion of the graphite to the substrate, but the resistance increased with the increasing amount of glass. The GGE with a weight ratio of 75:25 adheres well to the alumina and has a sheet resistance of 28 Ω/sq. Conductivity was then improved by printing an additional graphite layer over the GGE (GG-GE), resulting in a sheet resistance equivalent to graphite layer while maintaining adequate adhesion. These square structures were used as WE for a preliminary evaluation of the EC behaviour of these materials in a three-electrode configuration together with an Ag/AgCl reference electrode (RE) and a Pt sheet counter electrode (CE). Cyclic voltammetry was performed using 0,1 M phosphate buffer solution (PBS) with a pH of 7.0 as the supporting electrolyte and a 1mM solution of IMD dissolved in PBS as the analyte. The potential window of both WEs in PBS was at least between -1,2 V and 1,0 V. The reduction peak at -1,12 V and -1,05 V obtained in IMD solution on GGE and GG-GE, respectively, confirmed that these materials are suitable for IMD detection. Both materials were then used for preparation of WE in a miniature three-electrode configuration with all three electrodes integrated on an alumina substrate. WE was printed in the shape of a circle with a diameter of 4 mm and processed under the same conditions as before, while CE and RE were processed by screen printing and firing commercial Pt and Ag pastes, respectively. Preliminary EC characterization shows that these miniature systems are also suitable for the detection of IMD.

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Low temperature CO oxidation on lanthanum-iron doped strontium titanate (LFSTO): A perspective with operando ambient pressure NEXAFS spectroscopy

Mario Leopoldo Rivera Salazar,^{1*} Luca Braglia,² Silvia Mauri,² Aleksandr Petrov,² and Piero Torelli²

*marioleopoldo.riverasalazar@phd.units.it

¹ Università degli Studi di Trieste, Physics Department, P.le Europa 1, 34127 Trieste, Italy

² CNR-Istituto Officina dei Materiali, TASC, 34149 Trieste, Italy

Comprehending the processes involved in the CO oxidation has gained a lot of momentum in heterogenous catalysis not only from the environmental perspective with CO, but also for the potential suitability for other oxidation reactions, especially when this activity is observed at low temperatures^{1,2}. In this direction, different systems of transition metals (TM) supported on oxides¹ and perovskites^{3,4} had been explored, particularly noble TM (*e.g.* Au, Ag, Pt, Pd, Rh)^{4,5}. In some cases, the catalytic activity of these materials can be modified or enhanced with the addition of a dopant that modifies the electronic interactions between the active sites and the support material^{3,5}. Perovskites in particular, due to their unique structural properties and the redox behavior of its metal constituents have been widely studied as a photocatalyst with UV and visible light³. In this study, the CO oxidation mechanism on lanthanum-iron doped strontium titanate (LFSTO), was studied under and without the effects of a UV laser ($\lambda = 405$ nm) at 150°C. To follow the changes in the electronic structure and oxidation state of the TM (Ti, Fe), an operando ambient pressure NEXAFS spectroscopy was performed while the products of the reaction were monitored with a micro gas chromatograph (μ GC). The preliminary results demonstrate that LFSTO promote the oxidation of CO. While the laser illumination do not appear to have an important impact on the reaction, the role of the Fe dopant has been evidenced by operando soft-XAS spectroscopy.

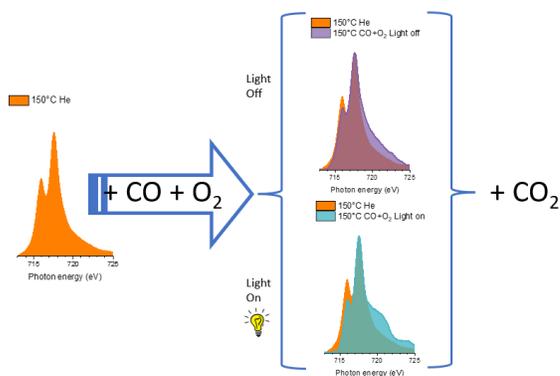


Figure 1. Fe L₃-edge in He at 150°C (left panel), and it's evolution during CO oxidation with no light excitation (upper right panel) and with light excitation (lower right panel).

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When carbon nanotubes meet self-organizing peptides

P. Rozhin,¹ S. Adorinni,¹ S. Kralj,² Brigitte Soula,³ E. Flauhaut,³ and S. Marchesan^{1*}

*smarchesan@units.it

¹ University of Trieste, Chem. Pharm. Sc. Dept., Trieste, Italy

² Jožef Stefan Institute, Materials Synthesis Dept., Ljubljana, Slovenia

³ Centre Interuniversitaire de Recherche et d'Ingénierie des Matériaux, Université P. Sabatier, 31062 Toulouse, France

Carbon nanotubes (CNTs) have raised scientists' interest for various uses, also in composite materials. In particular, the interaction between CNTs and proteins or peptides is of particular relevance to understand their fate in the environment and how biomolecules interact with CNTs, or even process CNTs.¹ Minimalistic self-assembling peptides can be attractive mimics of enzymes and offer insights into how biomolecules organized into functional structures during early stages of evolution.^{2,3} Furthermore, self-assembling peptides and nanocarbons can mutually interact and affect each other in interesting ways.^{4,5} In our laboratories, we previously analyzed how different nanocarbons interact with self-assembling peptides in aqueous environments, and found that nanocarbons' morphology affects the ability of peptides to coat the nanocarbons, and their propensity towards aggregation. In particular, multi-walled CNTs displayed ideal physico-chemical properties and an anisotropic morphology that led to their complete surface coating by the peptides, and to the formation of composite gels with self-healing ability.⁶ In our current investigations, we analyzed the case of single-walled and double-walled CNTs by using a plethora of techniques spanning from spectroscopic to microscopic analyses. We believe the emerging datasets could be useful to better understand how different types of CNTs interact with natural environments and affect biomolecules' structure and function.

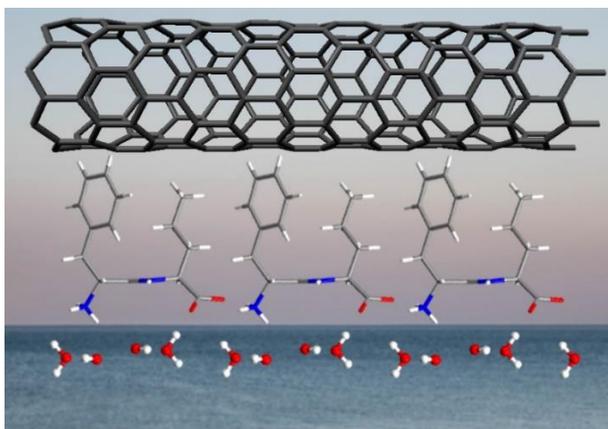


Figure 1. A self-assembling peptide exposes the hydrophobic surface to a CNT and the hydrophilic one to water.

Acknowledgements: The authors acknowledge COST Action EsSENce CA19118, supported by COST (European Cooperation in Science and Technology www.cost.eu).

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From carbon nanodots to protocells: versatile building blocks for novel biomimetic systems

Maria Sbacchi,^{1*} Pierangelo Gobbo,¹ and Maurizio Prato^{1,2,3}

*maria.sbacchi@phd.units.it

¹ Department of Chemical and Pharmaceutical Sciences, INSTM UdR Trieste, University of Trieste, via Licio Giorgieri 1, 34127 Trieste (Italy)

² CIC BiomaGUNE, (BRTA), 20014 Donostia-San Sebastián, Spain

³ Ikerbasque, Basque Foundation for Science, 48013 Bilbao, Spain

Carbon nanodots (CNDs) are quasi-spherical nanoparticles with a size below 10 nm and unique electronic features that can be readily synthesized from a wide range of carbon precursors. Moreover, their structure and properties can be finely tailored for specific applications, such as drug delivery, photocatalysis, and bioimaging.¹ Bottom-up synthetic biology is a field that has attracted increasing interest and which main focus has been the development of protocells, synthetic micro-encapsulated systems capable of mimicking some functions of living cells.² With the ultimate goal of bridging the gap between bottom-up synthetic biology and organic functional materials, the aim of this project is to develop novel protocell models by exploiting some appealing features of CNDs, such as low cost of the starting materials, biocompatibility, and intrinsic luminescence.

We developed a method to assemble the first CNDs-based colloidosomes, being protocell models made of colloidal particles as building blocks (Figure 1).²

To achieve this, the CNDs were made amphiphilic by grafting poly(*N*-isopropylacrylamide) (PNIPAAm) chains, synthesized *via* RAFT polymerisation. This process yielded CNDs/PNIPAAm nanoconjugates, which were subsequently used to assemble colloidosomes *via* the Pickering emulsion technique.² This was done by crosslinking the CNDs/PNIPAAm nanoconjugates into a continuous membrane at the oil/water droplet interface and transferring the colloidosomes in water. The synthesis of CNDs/PNIPAAm nanoconjugates was successful, as confirmed by NMR analysis and UV-Vis and fluorescence spectroscopy. These as-obtained colloidosomes formed highly stable Pickering emulsions, which were readily obtained and characterized by optical and fluorescence microscopy.

As a future outlook, we aim to develop the first rudimentary cell-like behaviours in these CNDs-based protocells and to integrate them into biomimetic systems.

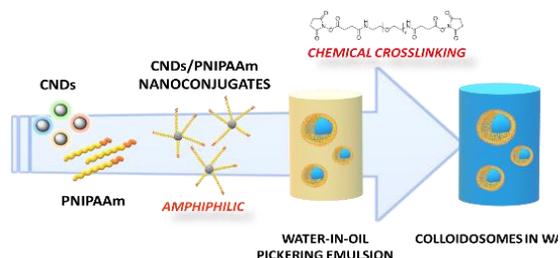


Figure 1. Outline of the synthesis of novel protocell membranes.

Acknowledgements: The author acknowledges the University of Trieste and the European Research Council (ERC AdG-2019 n°885323, e-DOTS).

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Photocatalytic reduction of CO₂ using semiconductor quantum dots and nanoarchitectonics

Syed Abdul Basit Shah,^{1*} and Vanni Lughi¹

*syedabdulbasit.shah@phd.units.it

¹ Department of Engineering and Architecture, Università degli Studi di Trieste

Green energy and sustainability have been the topic of interest for the past decade, considering the global warming and depleting energy reserves of coal and natural gas. Our study focuses on photocatalytic reduction of CO₂ and enhancing the stability of such systems, using nanostructures of II-VI semiconductors (CdSe, CdS), halide perovskites (MAPbBr₃, CsPbBr₃) synthesized using hot Injection method, ligand assisted reprecipitation (LARP) and successive ionic layer adsorption and reaction (SILAR), and characterized using x-ray diffraction, uv-vis spectroscopy, scanning electron microscopy and transmission electron microscopy to study the structural and optical properties. The size and optical response of nanostructures was tuned by varying the synthesis time. Ongoing activities involve growth and decoration of nanostructures onto titanium dioxide nano-powders and nanotubes to study the photocatalytic response, stability and charge carrier dynamics. Fossil fuels contribute to 80% of global energy demand [1] and generate carbon dioxide (CO₂) causing global climate degradation. Solar energy is a critical, free, everlasting and clean source, emerging as the most suitable and sustainable candidate for energy conversion and storage technologies [2], photocatalytic reduction utilizes this source and has the potential to subtract excess of CO₂ from atmosphere and produce carbon neutral fuels for tackling the current environmental issues.

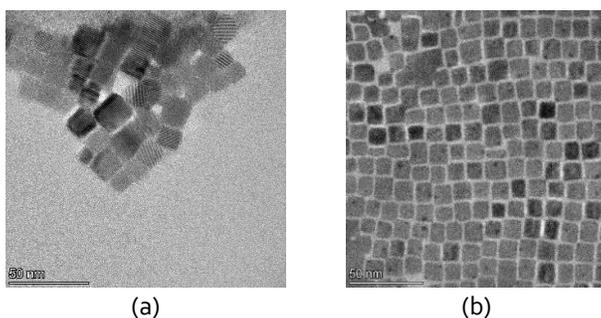


Figure 1. TEM images of (a) MAPbBr₃ prepared by LARP and (b) CsPbBr₃ by hot injection synthesis.

Acknowledgements: I would like to thank my supervisor Dr. Vanni Lughi, Dr. Christian Klink along with his research group 'nanostructures and nanomaterials' at University of Rostock, and Erasmus exchange for the one-month short-term exchange and ongoing 3 months research exchange.

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Ru catalyst modelling for ammonia synthesis

Luka Skubic,^{1,2} Sašo Gyergyek,² Blaž Likozar,³ and Matej Huš³

*luka.skubic@ijs.si

¹ Jožef Stefan Institut, Synthesis of Materials, Jamova cest 39, 1000 Ljubljana, Slovenia

² University of Maribor, Faculty of Chemistry and Chemical Engineering, Smetanova ulica 17, 2000 Maribor, Slovenia.

³ National Institute of Chemistry, Department of Catalysis and Chemical Reaction Engineering, Hajdrihova ulica 19, 1000 Ljubljana, Slovenia

Ammonia synthesis process, mostly commonly carried out as the Haber-Bosch process, is one of the largest energy consumers. Globally, 1-2 % of total energy supply is needed for ammonia production due to large pressures and temperatures needed. Iron-based catalysts were the first generation of catalysts used for the Haber-Bosch process and are still used on the industrial scale. Other transition metals are researched to obtain better reaction yields and selectivities and to perform the reaction under milder conditions. Recently, computational methods are gaining popularity for intelligent catalyst design. We studied ruthenium, which is known to be an efficient alternative for iron using density functional theory (DFT) and microkinetic modelling. [1, 2, 3]

First, we modelled a Ru slab to construct energy profiles and determine adsorption energies, most favorable adsorption sites and a detailed reaction mechanism. We used GPAW, where the wave function was described with plane waves (PW) with a cut-off energy of 450 eV and k-points sampling of $2 \times 2 \times 1$. We applied a dispersion correction (DFT-D3) and dipole correction. Furthermore, NEB calculations with the climbing image approach were used to determine transition states. Based on this data, the reaction was modelled on different Ru nanoparticles.

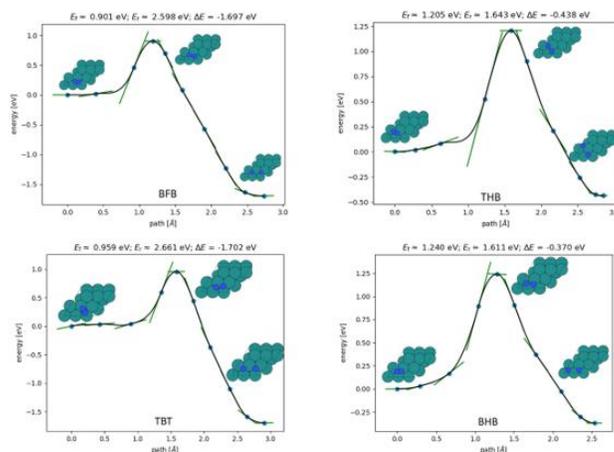


Figure 1. NEB calculations over different adsorption sites for ammonia synthesis using Ru (0001) catalyst.

Acknowledgments: This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 101022738.

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Development of a novel hybrid nanoplatform for theranostic applications in hepatocellular carcinoma (HCC)

Aharon Steffè,^{1,2*} Nicole Crestan,² Federica Di Cintio,¹ Monica Mossenta,¹ Davide Busato,¹ Marta Gambirasi,^{1,2} Idris Vruzhaj,^{1,3} Paolo Macor² Michele Dal Bo,¹ and Giuseppe Toffoli¹

*aharon.steffe@phd.units.it

¹Experimental and Clinical Pharmacology, Centro di Riferimento Oncologico di Aviano (CRO) IRCCS, Aviano, Italy

²Department of Life Sciences, University of Trieste, Trieste, Italy

³Department of Pharmaceutical and Pharmacological Sciences, University of Padua, Padua, Italy

Hepatocellular carcinoma (HCC) is the most common type of liver cancer and accounts for 90% of all cases worldwide, making it a global health challenge¹. Despite the diagnostic efforts made over decades, about 50% of all cases are diagnosed incidentally and when the tumor is already at the late stage dramatically limiting treatment options². Thus, there is the need to discover new tumor-associated antigens (TAAs) for the early diagnosis and the development of targeted therapies. In this context, glypican-3 (GPC-3) protein is not detected in healthy adult liver tissues but is overexpressed in 70-80% of patients suggesting its involvement in HCC. Moreover, nanomedicine has potential applications especially through the development of nanoparticles (NPs) that combine diagnostic and therapeutic abilities into a single platform (theranostics)³. As a result, the proposed approach was a nanosystem composed of an anti-GPC-3 antibody, a polymeric poly(lactic-co-glycolic acid) (PLGA) nanocarrier, and gold nanoparticles (GNPs). To begin with, GPC-3 protein expression was assessed in cancer cell lines, confirming the utility of GPC-3 as a suitable TAA for HCC. Hence, to obtain a specific anti-GPC-3 antibody, the production of IgG monoclonal antibodies was implemented leading to the selection of D8 antibody. PLGA nanocarrier was synthesised and characterized demonstrating excellent physicochemical properties, including a diameter around 250 nm, spherical nanocapsular morphology, thermal, pH and over time stability, absent cytotoxicity, and great ability to be internalized into HCC cells. GNPs of 14-15 nm were chemically produced and therefore encapsulated inside the PLGA-NPs core (hybrid NPs). The encapsulation process was confirmed by means of several complementary techniques. To test their contrasting ability, hybrid NPs were analyzed by X-ray Computed Tomography (CT) showing promising results in the potential to be distinguished from surroundings especially in a matrix mimicking the biological environment. Finally, hybrid NPs were functionalized with D8 antibody and *in vivo* investigated. When intravenously injected in HCC xenograft mouse model, following the biodistribution for 48h, targeted and untargeted hybrid NPs mainly accumulated in liver and spleen. However, D8 hybrid NPs exhibited a higher accumulation and retention in the tumor mass corroborating the benefit of an active cancer targeting approach. Despite the encouraging results, our nanosystem should be better characterized. Nevertheless, it lays the groundwork for potential *in vivo* applications in clinical setting.

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Electrocatalysis and photocatalysis: pathways for CO₂ reduction to fuels

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

Solving the energy crisis with zero CO₂ emission-based energy sources is the need of the hour, in addition to the overall reduction of CO₂ in the Earth's atmosphere. As an answer to both issues, obtaining fuels from photocatalysis and electrocatalysis of CO₂ reduction reaction (CO₂RR) is practical and a potent answer. However, CO₂ is an extremely stable molecule with C=O bond dissociation energy of ~750 kJ/mol which is much higher than that of some other chemical bonds like C-H (~430 kJ/mol) and C-C (~336 kJ/mol). This makes the CO₂ molecule require high input energy for its transformation to the various reduction products.¹ Heterogeneous photocatalysis/electrocatalysis is a viable pathway that can lower the overpotential making the reduction reactions feasible. In this work, catalysts with Z-scheme heterojunction have been synthesized with the aim to obtain suitable band positions and band gap for active photocatalysis. However, these same catalysts were tested for electrocatalytic CO₂RR and particularly bismuth-based catalysts were found to be active, among which BiOCl and its composites with g-C₃N₄ were seen to be selectively active for formate generation. Linear Sweep Voltammetry (LSV) studies performed in CO₂ and Argon saturated 0.1M KHCO₃ electrolyte with a scan rate of 5 mVs⁻¹ showed an increment in the current density in the former case which proved the activeness of the catalyst in CO₂RR. Several composites of BiOCl/g-C₃N₄ varying in their %'s were tested in a three-electrode gas-tight Dr. Bob cell™ connected to an online Gas Chromatography analyzer where the gaseous products were analyzed. The liquid products were analyzed after the Chronoamperometry by an Ionic Chromatography analyzer. Faradaic efficiencies (F.E.) accounted for 70% - 77% of formate production for the different composites and 52.1% BiOCl/g-C₃N₄ particularly formed 259 ppm of formate as compared to 231 ppm by the pristine BiOCl. As for photocatalysis, preliminary investigation with H₂ evolution tests have been carried out and CeO₂/g-C₃N₄ was found to be higher in its activity as compared to the pristine g-C₃N₄.

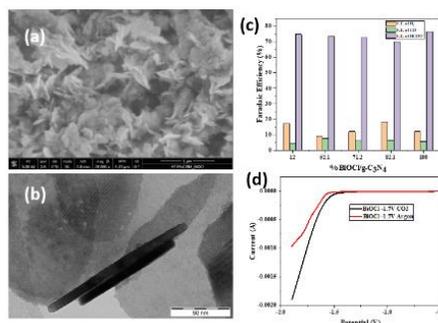


Figure 1. (a) SEM image of 52.1% BiOCl/g-C₃N₄ (b) TEM image of BiOCl showing nanosheet formation (c) F.E. of various %'s of composites (d) LSV graph of BiOCl in Ar and CO₂ atmosphere at -1.7V vs SCE.

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Exploring cardiac mechanobiology using nanotechnology

Michele Zanetti,^{1,2,3*} Brisa Pena Castellanos,³ Nicoletta Braidotti,^{1,2} Andrew Bonham,⁴ Suet-Nee Chen,³ Matthew R.G. Taylor,³ Orfeo Sbaizero,⁵ Luisa Mestroni,³ Laura Andolfi,² and Marco Lazzarino²

*zanetti@iom.cnr.it

¹ Department of Physics, University of Trieste, Trieste, Italy

² CNR-IOM, Istituto Officina dei Materiali, Consiglio Nazionale delle Ricerche, Trieste, Italy

³ Division of Cardiology, University of Colorado Denver Anschutz Medical Campus, Aurora, CO, USA

⁴ Department of Chemistry & Biochemistry, Metropolitan State University of Denver, Denver, CO, USA

⁵ Department of Engineering and Architecture, University of Trieste, Trieste, Italy

Cardiovascular diseases are the leading cause of death worldwide and the mechanical properties of the myocardium need to be extensively investigated to overcome this global epidemic. Two-dimensional (2D) and three-dimensional (3D) cell cultures allow a systematic manipulation and control of force dynamics, to address the myocardial multiscale organization and mechanobiology. Atomic Force Microscopy (AFM) can be used to uncover relevant mechanical fingerprints of diseased cardiomyocytes. As an example, our study of 2D cultures of Filamin C^{KO} cardiomyocytes showed impairments in cell stiffness and cell adhesion, as measured by AFM nanoindentation.

To investigate a physiological-like system, multicellular 3D cardiac spheroids (CSs) were later developed to bridge the gap between 2D cultures and the native heart tissue. Custom fabricated *Macro-cantilevers* were then fabricated and used to interrogate the CS whole mechanics (Figure 1).

After optimizing the AFM-based whole spheroid approach, a pathological complexity layer was added by investigating spheroids of co-cultured cardiomyocytes and fibroblasts to analyze the mechanical background of myocardial fibrosis (MF). In our study, fibrotic spheroids showed higher stiffnesses and impaired viscoelasticity, which are hallmarks of MF.

Finally, in the framework of a possible regeneration strategy, a Reverse Thermal Gel functionalized with gold nanoparticles (RTG-Au) was deployed as an electromechanical conditioning scaffold. CSs grown in conductive RTG-Au demonstrated advanced maturation levels as shown by the elevated gap junctions' expression, higher beating reactivity to AFM mechanical pacing and, in turn, higher twitch power.

Our results are likely to bring a positive impact on the study of heart regeneration and cardiovascular diseases, pushing towards unexplored avenues of cardiac mechanobiology through Nanotech-inspired bioengineering tools.

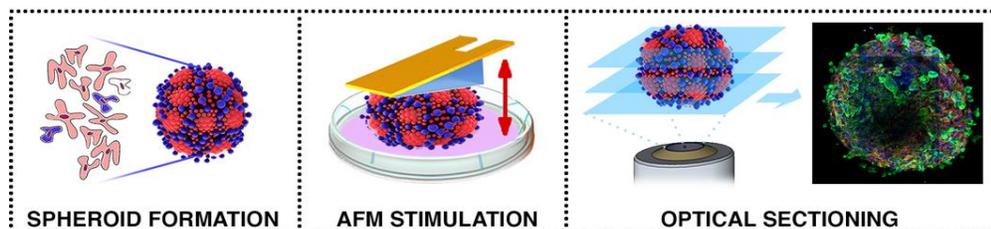


Figure 1
Illustrative schematic of some key steps regarding the 3D CSs experimental pipeline.

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Study of early interaction mechanism between asbestos fibers and cell proteins by microFITR and TEVC analysis

Martina Zangari,^{1,2*} Federica Piccirilli,² Annalisa Bernareggi,¹ Giuliano Zabucchi,¹ and Lisa Vaccari²

*martina.zangari@phd.units.it

¹ Dipartimento di Scienze della Vita, Università degli Studi di Trieste, Piazzale Europa, 34127 Trieste, Italy

² Sincrotrone Elettra Trieste, SISSI-Bio beamline, Area Science Park Basovizza, 34127 Trieste, Italy

Asbestos fibers inhalation is associated with severe lung diseases such as asbestosis and pleural mesothelioma (1). The comprehension of early interactions between asbestos fibers and cells is fundamental to understand the onset of asbestos-related diseases and to set up specific therapeutic approaches for the treatment of the exposed subjects. One essential process of pathogenesis is the interplay between fiber and proteins. Many proteins including ferritin (2), cytoskeletal proteins (3), and ion channels (4) bind the asbestos fibers. This kind of interaction can induce a significant increment of enzymatic activity, likely as a consequence of structural modifications of the absorbed protein (5). In the lung tissue, this process leads to the formation of asbestos bodies (AB, asbestos fiber coated with mucopolysaccharides and iron containing proteins) (6). The present contribution is focused on the study of the structural modifications of proteins following the fiber binding by FTIR microscopy, as well of the cell membrane using through two-electrode voltage clamp (TEVC) technique in *Xenopus leavis* oocytes. Firstly, we set up a protocol to reproduce an *in vitro* model of AB (AB-M) composed by holoferritin and three different asbestos fiber types (crocidolite, amosite and chrysotile). UV-Vis spectrophotometry and SDS page assay have shown that holoferritin interacts with chrysotile more avidly with respect to the other fibers. Interestingly, chrysotile contains only traces of iron as a contaminant (7) with respect to others. Holo/apo ferritin was incubated with chrysotile at pH 7.0 (cytoplasm) and 5.0 (phagosome) respectively for 2h, 48 h, and 1 week to study the secondary structure in a physiological environment. The FTIR microscopy analysis reveals aggregation of both proteins, but more intensely in apo than in holo. The aggregation was time depending and less dependent on pH. Preliminary results on *Xenopus leavis* oocytes revealed chrysotile able to modify the passive membrane properties, starting soon after incubation. In conclusion, our findings demonstrate that chrysotile affects the secondary structure of the proteins as well as the electrical proprieties of the cell membrane adding other possible contributions to the key mechanisms involved in the pathogenetic role played by this carcinogenic fiber.

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Effect of heat-treatment on microstructure and mechanical properties of thick films prepared by aerosol deposition

Katarina Žiberna,^{1,2,*} Matej Šadl,^{1,2} Aljaž Drnovšek,³
Goran Dražič,^{1,2,4} Hana Uršič,^{1,2} and Andreja Benčan,^{1,2}

*Katarina.Ziberna@ijs.si

¹ Electronic Ceramics Department, Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia

² Jožef Stefan International Postgraduate School, Jamova cesta 39, 1000 Ljubljana, Slovenia

³ Department of Thin Films and Surfaces, Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia

⁴ Department of Materials Chemistry, National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia

Aerosol deposition (AD) is an efficient method for producing thick films with high density at room temperature¹. The films grow by impact and fragmentation of the initial particles, which gives the films a unique microstructure². However, for electromechanically active materials, heat treatment after AD is still desirable to improve the dielectric, ferroelectric and energy storage properties, while annealing tends to degrade the mechanical properties³. The latter are rarely reported because the film thickness (usually up to a few tens of μm) presents an experimental challenge and limits the application of most mechanical tests.

In this contribution, we focus on the effects of thermal annealing on the microstructure and mechanical properties of $0.9\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.1\text{PbTiO}_3$ (PMN-10PT) thick films deposited on stainless steel using AD to gain better insight into the overall properties of the material. First, we investigate the effects of heat treatment at 500 °C on porosity, grain size, crystallinity, and crystallographic orientation using transmission electron microscopy down to the nm range. We also show that the substrate, stainless steel, is strongly affected by the heat treatment. In situ nanoindentation is then used to measure the mechanical properties of the as-prepared and annealed PMN-10PT films. The measured hardness and Young's modulus are discussed in terms of their distribution over the cross-section of the films.

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Toxicological assessment of nanoplastics in human macrophages by light and synchrotron techniques

Federica Zingaro,^{1,2*} Alessandra Gianoncelli,² Lorella Pascolo,³ and Giacomo Ceccone⁴

*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, 21027 Ispra (VA), Italy

The present work focuses on assessing the toxicological long-term nano plastics (NPs) exposure in *in vitro* human cell models. Although their usage has certainly revolutionized several fields, their detectable presence in water, food, human body compartments¹, addresses the scientific concerns.

Based on published evidence on NPs-human macrophages interactions in inflammatory response, we propose the use of a novel NPs model: polypropylene (PP) and polyvinyl chloride (PVC), labeled with CdSe-QDs², dispensed to polarized-monocytes macrophages (THP-1 cell line). Cell-NPs toxicological accumulation are investigated by X-ray imaging combined with fluorescence spectroscopy, Fourier-Transform Infrared Spectroscopy (FTIR) and standard bio-, chemical- techniques.

XRF elemental imaging analyses detected the different polymers (20, 50 µg/mL) NPs in macrophages by using the suitable excitation energy (1.7 keV) to track the emission of Se L-line of CdSe-QDs-NPs (TwinMic Beamline), in accordance with light fluorescence microscopy images (fig. 1a-b), instead 3.4 keV excitation energy (ID21 Beamline) allowed to trace the Cd of the QDs at nano-spatial resolution. Interestingly, we also observed an increased and co-localized Cl signal in the samples treated with PVC-NPs (contain Cl), (fig.1c). NPs exposure seems mainly affecting the cell lipid metabolism: macromolecular response investigated via FTIR showed a higher CO/Lipids and CH₂/CH₃ ratios in PP-cell treated cells compared with the control, clearly associated with lipidic peroxidation, oxidative stress, apoptotic vesicles formation. Instead, PVC-treated cells showed a reduced CH₂/CH₃ ratio, which can be assigned to the apoptosis, or cell membrane disruption³ (fig.1d). Moreover, lipid Droplets (LDs) formation at the cell membrane in PP-cells was observed by STXM morphological absorption images; in fact, LDs occur during the NPs phagocytosis mediated by macrophages, taking part to the innate immune response⁴ (fig.1e).

In conclusion, the proposed fluorescent NPs combined with advanced analytical techniques demonstrated to overcome the NPs chemical characterization issues in biological samples with the use of standard techniques. The present analyses revealed that although NPs did not exert significant direct effects on the cell viability, they are mainly involved in the lipid metabolisms impairment.

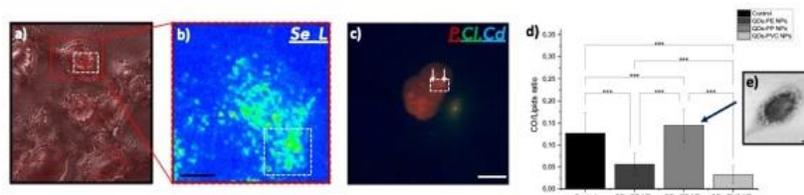


Figure 1. The light fluorescence image (a), Se XRF map (41µm × 41 µm, 1.7 keV photon energy at TwinMic beamline) (b), Cd XRF map (58µm × 50µm, 3.4 keV photon energy at ID21 beamline) (c) of PVC-NPs exposed cell. Box plot of relevant FTIR bands' ratios of ±NPs exposed cells (d) and STXM image of LDs (e). Scale bar is 10 µm.

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