Study with SERS spectroscopy of the nano-bio interface between biofluids and metal nanostructures.

A better understanding of the interaction between metal nanostructures, such as nanoparticles, and biological fluids (e.g. serum, saliva) is a necessary step toward the application of nanotechnology to biological systems, and in particular to human-related systems. Gold and silver nanoparticles and nanostructured surfaces could be used for a variety of applications, from photothermal therapy to drug delivery, from drug monitoring to diagnostics, as antibacterial agents or as sensors. Many of these applications require a direct contact between the nanostructured materials and the biofluid, so that a better insight on how the nano-objects interact with these complex biological samples is crucial.
However, while most studies presently available on the "nano-bio interface" are concerned with the role of proteins, especially in the formation of an adsorbed layer ("protein corona") on gold and silver nanoparticles, the interaction of small-molecules, such as metabolites, with the metal nanostructures ("non-protein corona") still needs to be examined and studied.
The reason of this delay has been the lack of experimental techniques capable to investigate small molecules adsorbed on metal surfaces in the context of complex samples, as biofluids are. Surface-Enhanced Raman Spectroscopy (SERS) is an analytical technique capable of detecting the vibrational spectra of species adsorbed on nanostructured metal surfaces, and thus it is a very promising tool to identify adsorbed metabolites.
PhD candidates will use SERS to study the interaction of different biofluids (starting from model solutions of proteins and metabolites) with gold and silver nanoparticles and nanostructured surfaces. Besides SERS, other techniques will be used, also in collaboration with other centers, to characterize the nanostructures and the nano-biointerface: electron microscopy (TEM, SEM), Dynamic Light Scattering, and FT-IR among others. While studying the nano-bio interface and based on their findings, candidates will be also encouraged to explore possible bioanalytical or clinical applications.

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PhD position 2019 - Prof. Maurizio Prato

Smart composites for tissue engineering applications

Carbon nanotubes are able to promote and enhance the growth and the functional activity of some classes of electrically active cells, namely neurons and cardiomyocytes. In part of our research group, we focus on the production of carbon nanomaterial-based composites for applications as substrates for the regeneration of neuronal and cardiac tissues. In particular, our research work is currently considering spongy composite materials made of carbon nanotubes and polymethyldisiloxane (PDMS), whose features of conductivity, porosity and stiffness make them ideal for hosting electroactive cells [Sci Rep, 2015, 956, Sci. Adv. 2016, 2, e1600087]. The work is developed in close collaborations with neurobiologists and cardiobiologists in Italy and abroad (mainly Spain and USA).

The PhD candidate will explore further the potential of these materials, studying how any changes in their physical properties (porosity, stiffness, size) can tune the ability of cell sustaining. New cell types will be considered (stem cells for example) in addition to those already under evaluation. Furthermore, the PhD student will try to enrich these composites with molecules able to promote further the growth, the functionality and the maturation of these cells. At the same time, other classes of biocompatible polymers will be taken into consideration, like polysaccharides, polyhydroxyalkanoates and proteins. As carbon nanomaterial, also graphene, that is currently an emerging material in several fields of application, will be considered for its outstanding chemical and physical properties.

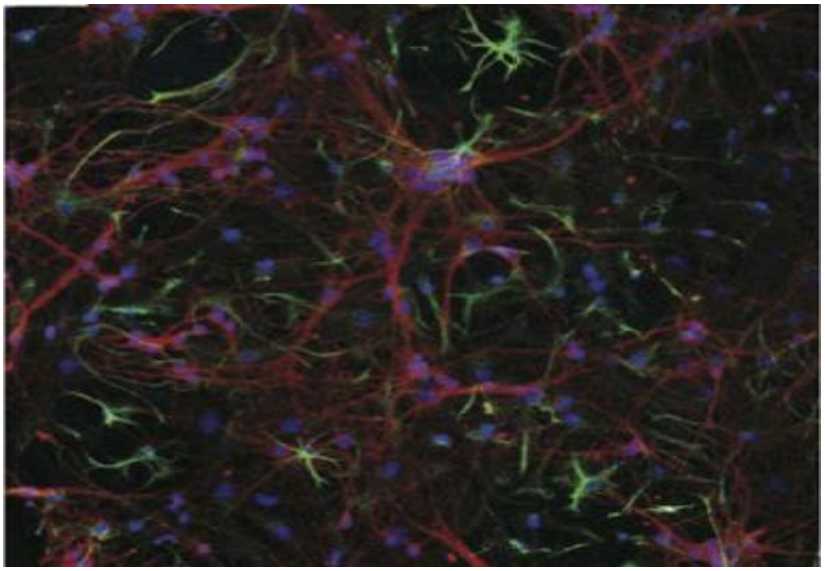

Figure. Confocal microscope image of hippocampal cell cultures grown into 3D PDMS-carbon nanotube sponge (neurons in red, glia cells in green, nuclei of both cells in blue)

The PhD student will work in a multidisciplinary environment where organic chemistry, materials chemistry and cell biology are closely interconnected. He/she will be required to have a high level of scientific curiosity and to be prone to face new challenges. He/she should be interested both in chemistry and biology with an open eye on medicine. He/she will work in an equipped chemical laboratory and will take advantage of analytical techniques like ultraviolet spectroscopy, infrared spectrophotometry, fluorimetry, thermogravimetric analysis, differential scanning calorimetry, atomic force microscopy, transmission electron microscopy. Short and long stages in foreign countries will also be considered, according to the student's doctoral program.

Out-of-equilibrium peptide self-assembly

Supervisor: Prof. Silvia Marchesan

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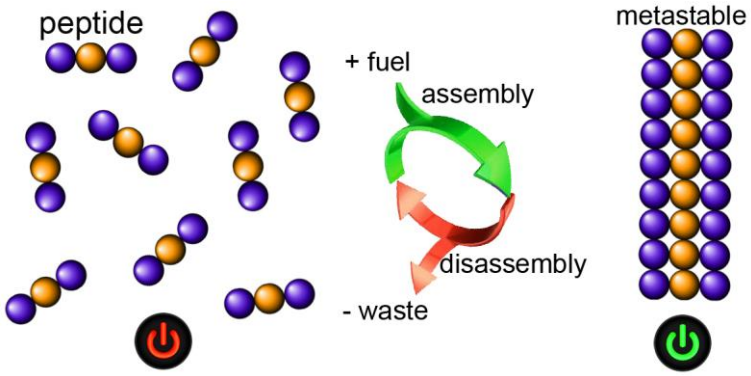
Life processes occur far from equilibrium, with living organisms being composed of supramolecular systems that adapt to the environment.[1] In particular, proteins exert very fascinating functions, that span from the synthesis of biomolecules, to transport and cell movement.

Minimalistic peptides can be attractive protein mimics that are low-cost and offer great chemical diversity to achieve different functions.[2] Upon design, they can self-organize into structures that span from the nano- to the macroscopic scale – thus forming nanostructured, functional materials that we can see by eye.[2,3] The desired function can be switched on/off with assembly/disassembly.

This ability, coupled to chemical reactions that yield metastable products, opens the way to the design of complex, multifunctional systems that can evolve over time and adapt to the environment.[4] In this manner, we can envisage smart dynamic systems that respond *ad hoc* to chemical stimuli and potentially participate in chemical cascades to exert more complex functions.



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Nanodiamonds in Theranostics

Supervisor: Tatiana Da Ros

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Nanodiamonds (NDs) could be considered the oldest carbon-based nanomaterials as they were discovered many years ago but their popularity is quid recent, with the development of nanotechnology. They have an sp^3 diamond core and their surface is generally present a mixture of sp^2 and sp^3 hybridized atoms. The possible surface groups of pristine materials are characterized as ketone, aldehyde, carboxylic acid, ester, anhydride, cyclic ketone, lactone, amine, epoxide, etc., so various surface functionalizations could be performed in order to introduce new biological and electronic properties.[1] According to the primary particle size, NDs can be classified in three main groups: nanocrystalline diamond particulate (10-100 nm), ultrananocrystalline diamond particulate (0-10 nm), diamondoids (~1 to ~2 nm).[2] Among these, ultrananocrystalline diamonds are the most promising nanomaterials for microelectronics, biotechnology and medical applications, in particular when mean size is 4-5 nm.

Nanodiamonds are chemically and physically stable nanomaterials, but their surface can be chemically modified for various purposes. They present some properties of bulk diamond (high Young's modulus and mechanical strength, high thermal conductivity), but also better characteristics: good dispersibility, high adsorption ability, solid lubricating ability and biocompatibility.[3] Thanks to the large variety of surface groups, different functionalizations could be performed and many different surface groups can be attached on NDs using wet chemistry methods[4] and a variety of molecules with valuable properties (biological, fluorescence etc.) can be introduced for example by amidation on ND–COOH.

NDs may be used for a broad range of applications such as mechanical applications, electrochemical applications and medical purposes and in this respect various derivatization methodologies will be optimized and dedicate to the preparation of derivatives with theranostic applications.

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Prof Paolo Fornasiero

Catalysis for an efficient utilization of carbon resources

The project will, in fundamental science, investigate the catalytic conversion of C1 small molecules (methane, carbon dioxide, etc.) and biomass macromolecules (cellulose, hemicellulose, lignin and their derived platform molecules). It is expected to design new catalytic materials, typically single-atom and single-site catalysts, and to provide fundamental understanding of confined catalysis effect. Efforts will be devoted to the development of new strategies for the selective cleavage of C-C and C-O bonds in the biomass molecules for the sustainable production of renewable fuels and chemicals. Thermal, photo- and electro- chemical activation will be considered. The ultimate goal is to build a world-class multi-integrated research platform of both catalytic materials and reaction engineering towards addressing the key challenges in the catalytic conversion of carbon resources, and in the end to contribute to the significant improvement in the utilization efficiency of carbon resources.

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CONTROL OF SELF-ASSEMBLY OF FUNCTIONAL GOLD NANOPARTICLES

Supervision: Lucia Pasquato and Paolo Pengo, Department of Chemical and Pharmaceutical Sciences, University of Trieste, e-mail: lpasquato@units.it, ppengo@units.it

Directed self-assembly of nanometer-sized materials into ordered arrays are the most widely studied targets of current research. The bottom-up approach for the fabrication of functional materials is very attractive since it utilizes small and rather simple building blocks that will self-assemble into larger, more complex nanostructures. For these approaches, (bio)chemists are inspired by Mother Nature, who uses a large variety of covalent and non-covalent interaction mechanisms. In this context we are interested in developing new protocols to self-assemble anisotropic hybrid organic-inorganic nanoparticles with a control over the assembly process to give rise to well defined architectures. Particularly interesting will be to trigger the assembly/disassembly process upon application of external chemical stimuli. The project foresees the design and synthesis of anisotropic gold nanoparticles, their modification with selected functional groups and/or functional building blocks and the study of their self-assembling process driven by different conditions. A variety of techniques will be used to characterize the final material and to investigate their optical and electronic properties.

The ideal candidate should be highly talented and very motivated with skills in organic synthesis and spectroscopy techniques.

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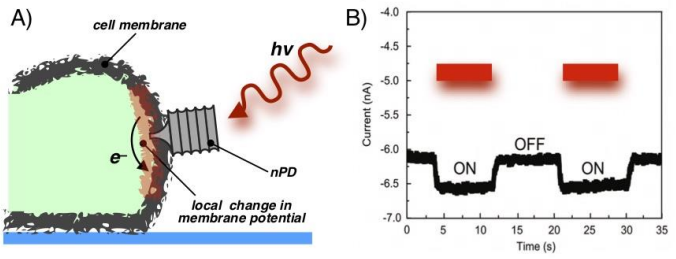
Smart nanodevices for optical modulation of 2D/3D neuronal network activity.



Interaction of nanoscale photodiodes (nPD) with the cell membrane. *A) scheme depicting nPD working principle: light stimulation will induce a local perturbation of cell membrane potential propagating from nPD insertion point; B) dynamic photocurrent response with a periodically "on-off" white-LED lamp, at 0 V bias.*

The project proposes, within an HFSP action, to study neuronal cells excitability through a new class of nanoscale photodiodes (nPD), able to generate current upon illumination, which can control neural circuits at the single cell or sub-cellular level [1]. These nanodevices will be biochemically functionalized to target specific neurons and used to evaluate the emergence of triggered dynamic activity and synaptic plastic phenomena at the nanoscale in 2D and 3D systems [2].

Initially, flat neuronal networks will be studied to highlight nPD ability to induce or avoid neuronal activation in a precise spatiotemporal way. Subsequently, we would take advantage of 3D neuronal networks developed into a supporting synthetic scaffold [3] to validate nPD neuromodulation ability in a complex 3D system. Network morphology and activity would be studied at sub-single cell level employing confocal/2-photons microscopy and calcium-imaging experiments [3]. The resulting hybrid system will allow new investigations of the interaction taking place between synthetic (nano)materials and cell membranes, highlighting new strategies to modulate neuronal network activity.

The project proposes to bridge together (nano)material science, biochemistry, and neuroscience through a close, and unique, interdisciplinary collaboration.

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Reference person: Dr. Denis Scaini (dscaini@sissa.it)

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Research Topic: Charge transfer processs in complex interfaces.

Supervision:

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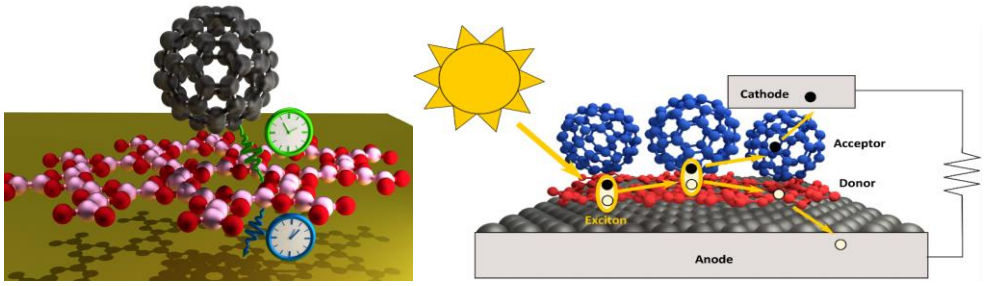
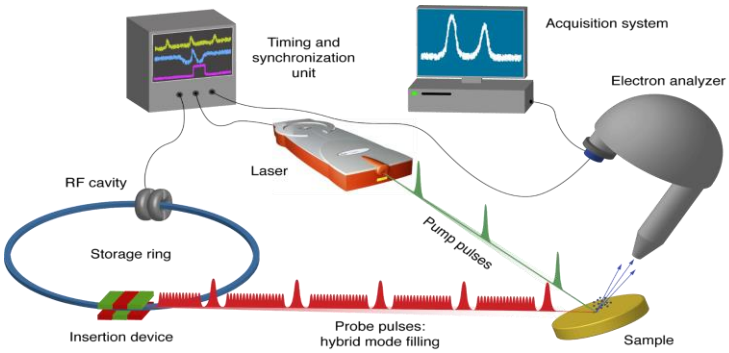


There is a dramatic raise in the scientific and technological interest for new complex 2D materials that extend substantially the graphene family (2D dichalcogenides, phosphorene, hexagonal boron nitride hBN etc), their combination in stacked heterostructures, 2D Covalent Organic Frameworks (COF) and more complex hybrid materials that incorporate also organic molecules. In devices based on these materials, interface processes are ubiquitous and critical for the efficiency much more than when traditional materials are employed. Furthermore the interposition of a 2D templating architecture between electrodes and the organic layers represents a powerful tool for the improvement of the overall device performances. Therefore, there is an increasing interest in the synthesis and characterization of possible 2D templates able to tailor the electronic properties of complex Metal/Template/Organic (MTO) architectures. Possible templates we are interested in range from functionalized 2D materials, to Covalent Organic Frameworks, to self-assembled monolayers of organic molecules. Major efforts have been made in last years to study the morphology of these systems, while their electronic properties are in most cases only partially described. There is a need therefore for a deeper understanding and control of processes like charge transfer at interfaces between the different components in complex materials and in MTO architectures. Charge injection across molecular junctions can occur at the femto- to nanosecond time scales. We combine different time resolved spectroscopic techniques (pump-probe spectroscopy using femto laser or Free Electron Lasers, X-ray Resonant Photoemission spectroscopy) to investigate the electronic properties in MTO hetero-structures, revealing the charge dynamics in both directions (to/from the molecule) at these complex interfaces.

The research program is part of the recently financed project MIUR PRIN: FERMAT Fast ElectRon dynamics in novel hybrid organic-2D MATerials and will be carried out in collaboration with various international research groups based in USA (Columbia University), Slovenia etc

The student will have access to newly installed experimental apparatuses for Time resolved spectroscopies and Synchrotron radiation experiments.



Penetration of metal nanoparticles through oral mucosa

Supervisor: prof. Francesca Larese Filon

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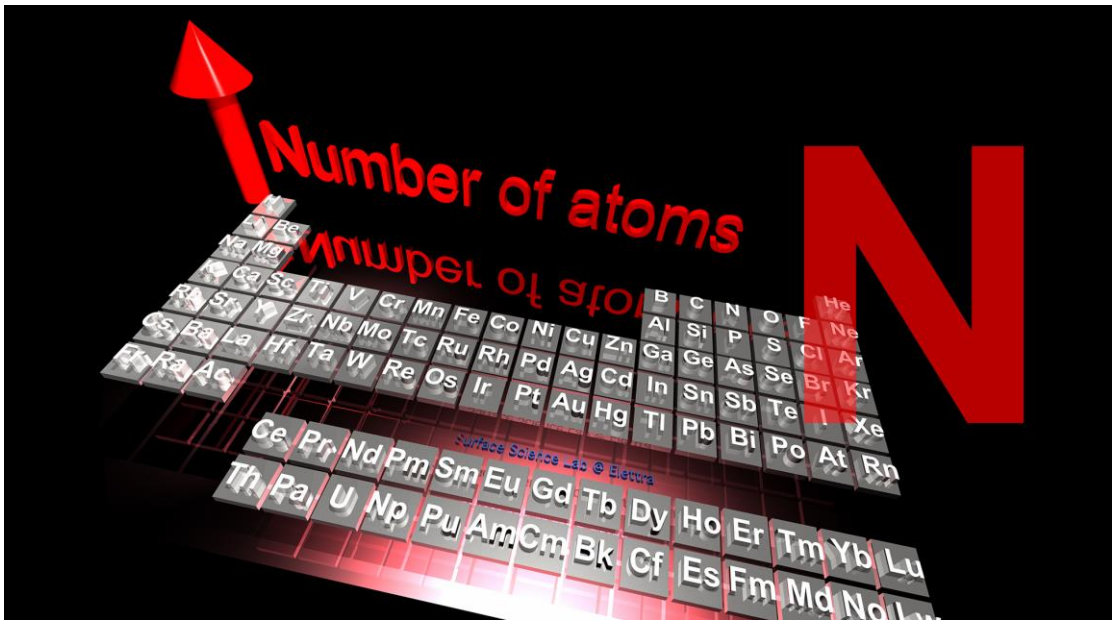
The project aims to study oral mucosa penetration of metal nanoparticles (NP) using an ex-vivo approach. Consumers are exposed to foods, oral solutions, toothpastes containing NP, workers can contaminate the oral mucosa with dirty hands when handling NP, however it is not clear if NP could pass through oral mucosa as NP or as ions released from NP themselves. The "translocation" of NP through biological membranes has been suggested but there is the need to confirm the amount of this phenomenon in in-vivo condition. Moreover, data on oral mucosa NP absorption will be important for drug delivery. The NP penetration and permeation (the NP capability to cross the membrane) of silver, titania and aluminium oxide NP will be studied using the Franz-cells methods and pig oral mucosa.

Advanced chemical analysis will permit to detect single particles in receiving phases and to compare ions and NP permeating the oral mucosa.

Exploring a *new dimension* of the periodic table

How the behaviour of a material evolves as it built up atom by atom from the monomer to the bulk has been a fascinating question from the time of ancient Greek philosophers who were the firsts to propose the concept of atoms as the smallest indivisible units of a substance.
When we reach the nanoscale things become very intriguing: a very small cluster of atoms can drastically change its properties by adding or removing just a single atom. We are in the regime of non-scalable properties.
The goal of our research team is to understand how structural, electronic, magnetic and chemical properties evolve atom by atom, from the monomer to the bulk.
ENAC, the newly developed size-selected cluster source of the Surface Science Laboratory at Elettra, capable to produce clusters formed by an exact number N of atoms, is the key experimental tool to reach our goal. We will do it by coupling the clusters with the new familes of 2D materials we are working with since long time. The new set-up, in combination with the synchrotron light of Elettra, represents a truly unique system worldwide in the field of experimental condensed matter physics.



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