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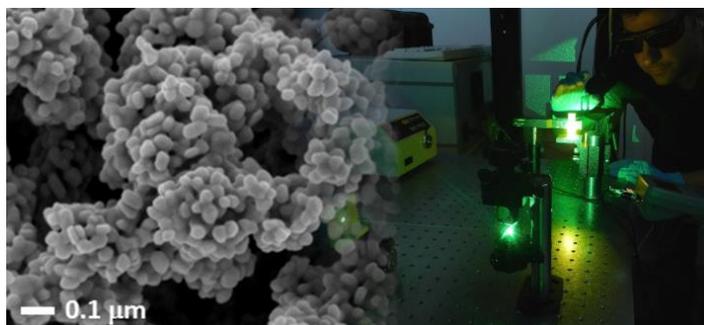
Candidates applying for M/1 scholarship may carry out their activity in any of the research groups active within the PhD program in Nanotechnology.

The research groups can be found [here](#). Please contact the group leader to enquire about the possibility of a PhD position for the A.Y. 2021/2022.

There are also specific research projects available for candidates applying for M/1 scholarship. These are presented in the following pages.

Exploring the *nano-bio interface* with SERS spectroscopy in view of clinical applications of metal nanostructures.

prof. Alois BONIFACIO (supervisor), prof. Valter SERGO



A better understanding of the interaction between metal nanostructures, such as metal nanoparticles, and biological fluids (e.g. serum, saliva) is a necessary step toward the application of nanotechnology to biological systems, and in particular to humans. Gold and silver nanoparticles and other nanostructured surfaces are promising for a variety of applications, from photo-thermal therapy to drug delivery, from drug monitoring to diagnostics, as antibacterial agents or as sensors. Many of these application require the direct contact between these nanomaterials and a biofluid, so that a better insight on how there nano-objects interact with these complex biological samples is crucial.

While most studies on the “nano-bio interface” concerned 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 metal nanostructures (“non-protein corona”) still needs to be studied.

The reason of this delay has been the lack of experimental techniques able to investigate small molecules adsorbed on these metal surfaces in the context of chemically complex samples, such as biofluids. Surface-Enhanced Raman Spectroscopy (SERS) is an analytical technique capable of detecting the vibrational spectra of species adsorbed on nanostructured metal surfaces, and thus to identify adsorbed metabolites.

Candidates will use SERS to study the interaction of different biofluids, starting from model solutions or proteins and metabolites, with gold and silver nanoparticles and nanostructured surfaces. Besides SERS, other techniques will be used to characterize the nanostructures and the nano-bio interface, also in collaboration with other centers, such as electron microscopy (TEM, SEM), Dynamic Light Scattering (DLS), and FT-IR among others. While studying the nano-bio interface, candidates will be also encouraged to explore and develop possible bioanalytical or clinical applications relying on their findings.

Short Bibliography

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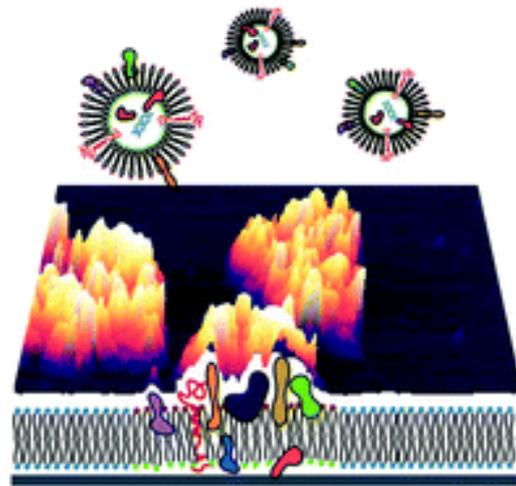
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Gurian E., Giraudi P., Rosso N., Tiribelli C., Bonazza D., Zanconati F., Giuricin M., Palmisano S., De Manzini N., Sergio V., Bonifacio A., *Differentiation between stages of non-alcoholic fatty liver diseases using surface-enhanced Raman spectroscopy* (2020), *Analytica Chimica Acta*, 1110, pp. 190-198.

Characterization of membrane proteins in natural environment with focus on metastatic breast cancer

Membrane-proteins structure and function are directly related to the interactions with the complex, highly dynamic structure and morphology of the lipid bilayer in which they are embedded. One way to preserve such interactions is to reconstitute the proteins into artificial lipid bilayers. This offers the advantage of a simple model, compatible with many surface characterization techniques¹. However, the natural protein topology inside artificial systems is not guaranteed. To overcome this problem, membrane proteins can be obtained from natural, giant plasma membrane vesicles (GPMV) produced directly from cells via chemical blebbing methods². In a recent paper it has been shown that when deposited on glass substrates GPMV will undergo a rupture exposing their intracellular side to the liquid cell and that, by playing with relative surface affinities, the deposited layer can be transferred into another substrate exposing in this way the extracellular side of the membrane, making both sides of the transmembrane protein available to the characterization³.



and that, by playing with relative surface affinities, the deposited layer can be transferred into another substrate exposing in this way the extracellular side of the membrane, making both sides of the transmembrane protein available to the characterization³. In this project, we plan to combine standard biochemical tools, Atomic Force Microscopy and Spectroscopy, Fluorescence Microscopies modes (TIRF, total internal reflection fluorescence, FRET, Forster Resonance Energy Transfer, FRAP, Fluorescence Recovery After Photobleaching), Quartz Crystal Microbalance, X-ray and neutron scattering techniques (also applied to the GPMV in liquid solution) and nano-IR (infrared) vibrational spectroscopies to characterize the properties of the natural lipid environment (e.g. lipid composition in each leaflet, amount and dynamics of cholesterol and its role in membrane fluidity, etc.) in the case of vesicles produced by breast cancer cell lines of different metastatic potential. In particular, we will focus on the HER2 (human epidermal growth factor receptor 2) dynamics and on the interactions with the lipids in the membrane and with scaffolding proteins as caveolin, a mechanical-stress protectors of cell membranes, and flotillin, a receptor-stabilizer in lipid rafts, also used as a potential predictor of prognosis in breast cancer patients, to highlight possible novel targets for anticancer therapy.

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Loredana Casalis and Pietro Parisse, NanoInnovation Lab Elettra and CNR-IOM
In collaboration with **Valeria Rondelli**, Università degli studi di Milano

Development of metal-free photocatalysts for advanced photocatalytic organic synthesis

Supervisor: Prof Paolo Fornasiero (Università di Trieste)

Co-Supervisor: Prof. M. Prato, Dr. G. Filippini and Dr. Michele Melchionna

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Heterogeneous photocatalysis by metal-free catalysts is an exceptionally attractive field, fitting most of the criteria of “green chemistry” modern philosophy, where integrating all-around sustainability aspects into chemical production is the primary objective. Despite the promising findings and the high expectations for the use of metal-free materials as photocatalysts for organic transformations, the full potential of these catalysts has yet to be uncovered. Particular interest is drawn by organic reactions featuring C-C and C-X (X = non-metal atom) couplings, and very recent findings demonstrate the ability of non-metallic carbon nitride semiconductors to catalyze such types of reactions with high activity and versatility.^[1] However, fast progresses hinge on the development of advanced methodologies to define structure/activity relationship, thus unveiling the mechanism of the catalytic cycle of the particular organic reaction. This will guide rational design of materials with suitable structural, chemical and electronic properties to trigger photocatalytic reaction of relevance. Recent achievements by our group showed that a range of ad hoc post-synthetic modifications of carbon nitride could cause diversification of catalytic behavior towards C–C bond formation toward perfluoroalkylated compounds.^[2] Important parameters such as bandgap, porosity, and binding affinity towards the reactive substrate could be tuned by the specific modification, with important catalytic consequences, as confirmed by advanced NMR techniques.

The research activity of this project will focus on the design of new visible light-responsive metal-free semiconductors able to catalyse various organic transformations relevant for industrial applications. The PhD candidate will have the opportunity to work in both material synthesis and characterization and organic chemistry, ingeniously developing various synthetic strategies for materials to address different types of photocatalytic organic reactions. State-of-the-art material science will be used to endow the catalyst with boosted performance, by exploring: 1) the implementation of Z-Scheme for photocatalysis interfacing two semiconductor materials, 2) conducting opportune chemical modification (doping), 3) effecting controlled structural modifications, 4) creating the premises for dual-catalysis reactions through combination with metal complexes (figure 1) An ambitious ultimate target will be the exploitation of the new materials in total synthesis of biologically active molecules.

In addition to a rich arsenal of synthetic methods for materials assembly, as well as for organic reactions, the PhD candidate will acquire deep knowledge on advanced spectroscopic techniques and microscopy, with the chance to collaborate with internationally recognized experts in materials science, catalysis and characterization.

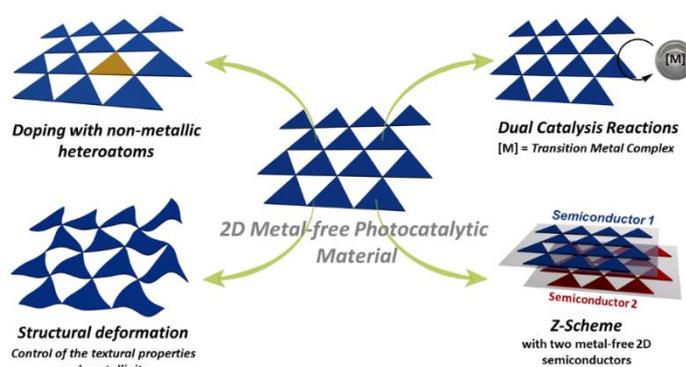


Figure 1. Envisioned avenues for the development of metal-free photocatalysts for organic synthesis

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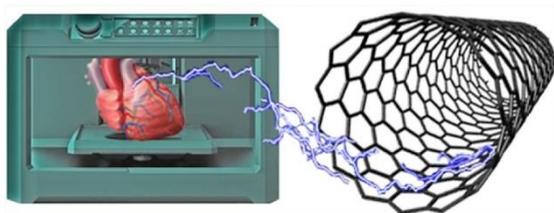
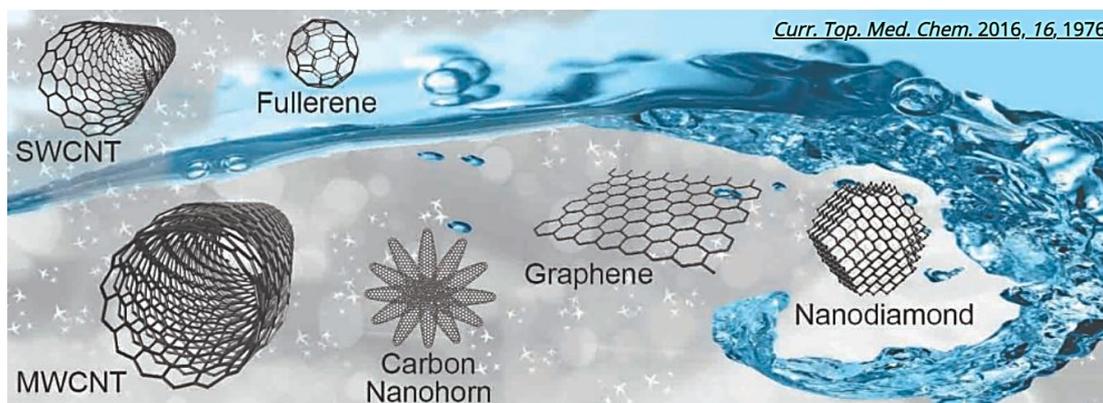
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NANOSTRUCTURED BIOMATERIALS for MEDICINE

Supervisor: Prof. S. Marchesan www.marchesalab.com

Carbon nanostructures (*e.g.*, graphene, carbon nanotubes) are extraordinary nanomaterials with unique physico-chemical properties, such as high conductivity, low density, high robustness, and ability to respond to near infrared light irradiation, all of which give them a high potential to innovate in medicine.¹ They can undergo chemical functionalization, thus it is possible to fine-tune their properties as need depending on the intended application, for instance to render them water-dispersible and to facilitate the formation of composite or hybrid materials.^{2,3} They are particularly attractive to reconstruct conductive tissues, such as the heart⁴ and the nerve tissue,⁵ but are also convenient scaffolds for advanced diagnostics, for instance for cancer detection.⁶ For applications in the health sector, it can be convenient to couple them with biomolecules, and embed them in a soft hydrogel matrix to favour interactions with cells.⁷ In particular, self-assembling short peptides are very interesting building blocks that not only can yield biocompatible hydrogels,⁸⁻¹⁰ but can also interact favourable with carbon nanostructures, which can add further properties, such as self-healing behaviour.¹¹

Research in this hot area will involve the functionalization and characterization of nanocarbons and their conjugation with short self-assembling peptides and other biomolecules to achieve the next-generation biomaterials to repair human tissues, or to allow advanced diagnostics. The research is highly multidisciplinary, entailing diverse *in silico* and experimental techniques that encompass the areas of chemistry, biology, and physics, and that will include synchrotron-radiation techniques.



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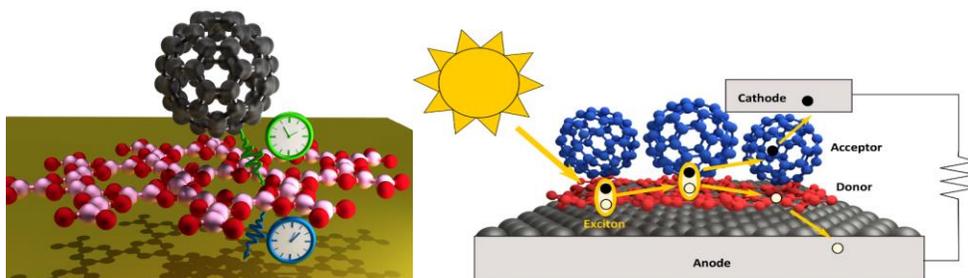
Research Topic: Charge transfer process in complex interfaces

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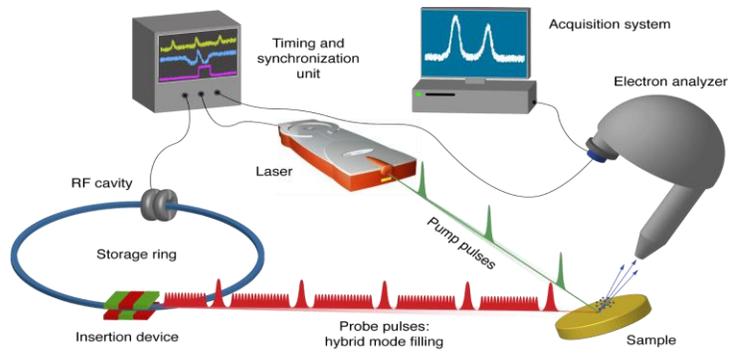
Alberto Morgante (Physics Department, University of Trieste, and CNR-IOM Laboratorio TASC), e-mail: amorgante@units.it



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.



EXPLORING THE MULTIDIMENSIONAL COMPLEXITY OF SELF-ASSEMBLED MONOLAYER PROTECTED METAL NANOPARTICLES BY ADVANCED COMPUTATIONAL TECHNIQUES

Supervisor: Paola Posocco (University of Trieste)

The chemistry of surface-stabilizing species plays a critical role in determining the properties, interactions and reactions of myriad nanomaterials, including the archetypal self-assembled monolayer-stabilized gold nanoparticles (SAM-AuNPs). While experimental efforts have led to significant developments in synthesis and functionality, harnessing the technological potential of these nanomaterials demands that we extend to nanoscale chemical entities the predictive structure–function correlations currently taken for granted in the molecular world.

The distinct surface-bound environment imposes very specific conditions on molecular reactivity and interactions. The parameter space that defines the interfacial environment at the surface of colloidal nanomaterials is far more complex than that typically encountered for bulk solution systems. Molecular and nanoscale parameters influence numerous other structural and physicochemical features. In turn, each of these will affect interactions and reactions at the nanoparticle–molecule–solvent interface. This complexity presents a huge unmet challenge.

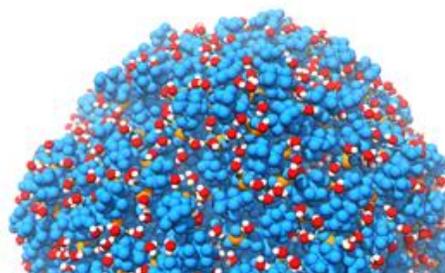
Developing *ad hoc* computational models and combining them with advanced computational techniques will allow us to reveal not only unprecedented details on molecular structures in isolation, but also to consider the emergent consequences of confining several molecules on a nanoparticle surface and the collective interactions between many nanoparticles at the same time.

This will pave the way to a new era of chemistry incorporating nanoscale building blocks that is just as predictable as present-day chemical technology based on molecules. Furthermore, SAM-AuNPs provide a general platform for studying surface chemistry, which is critical to many applications, from (bio)sensors and heterogeneous catalysts to hierarchically, molecularly-controlled, and reconfigurable 3D assemblies.

In this context, the PhD activity will focus on the development of new computational models of a variety of SAM-AuNPs. The main goal is to understand the key molecular factors, forces and properties that control self-assembly, structure, reaction and recognition properties of SAM-AuNPs. Via the integration of many technique (e.g. quantum mechanics, atomistic and coarse-grained dynamics) and the use of classical and advanced molecular simulation approaches (e.g., molecular dynamics, enhanced sampling techniques such as metadynamics, thermodynamics integration, etc.), the selected PhD candidate will investigate structure and behavior of SAM-AuNPs on a wide spatio-temporal scale.

We are seeking people with:

- experience in molecular modelling and common packages (e.g. LAMMPS, GROMACS, AMBER)
- programming skills (preferably Python or C++) and knowledge of parallel computing environment
- strong motivation and enthusiasm for research
- good attitude to work in team
- good written and spoken English



Self-assembled monolayer on a spherical nanoparticle and selected bonded water molecules.

Have a look at these references:

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Do not hesitate to write for any further information!

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Catalytic Valorization of Phenols

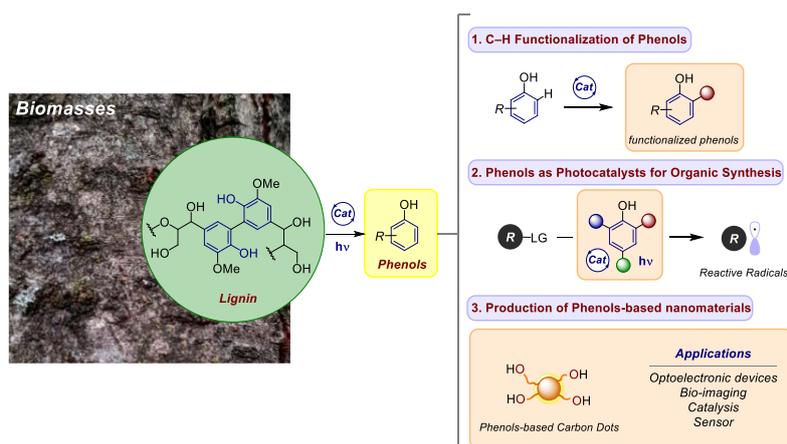
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This project aims at designing novel (photo)catalytic methods for both the production of phenols from biomasses as well as for their chemical derivatization.

Phenols are extremely relevant chemical functionalities in natural, synthetic and industrial chemistry. Therefore, the utilization of renewable biomasses (e.g., lignin) to economically produce phenol derivatives is of great significance.^[1] Within this context, it has been shown that carbon nitrides (CNs) are capable of selectively catalyzing the C-C bond cleavage in lignin models under visible light irradiation.^[2] In addition, the development of new catalytic approaches for the directed C-H functionalization of lignin-derived phenols has become a matter of paramount importance.^[3] Phenolic compounds have been also used as catalysts in organic synthesis to photochemically initiate important radical transformations. Lastly, these phenols may be employed as inexpensive molecular precursors for producing valuable water soluble carbon-based nanoparticles, namely carbon dots.^[4]



Our first objective is to develop novel efficient CNs-based catalysts for the light-driven depolymerization of native lignin. We also aim to develop novel chemical methodologies for either the direct C-H functionalization of lignin-derived phenols or to employ them as photocatalysts to produce reactive open-shell species. Besides, the student will deal with the synthesis of novel carbon dots starting from lignin-derived phenolic compounds. In this way, the PhD student will become fluent in organic synthesis, catalysis and materials science. The PhD student will build on the work already in progress within the group and will have the opportunity to express his/her individual interests and skills in shaping the development of his/her path into research.

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