# NOTE

Candidates applying for the scholarship 1 may carry out their activity in any of the research area active within the PhD program in Nanotechnology. These can be found <u>here</u>.

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

# Synthesis and characterization of functionalized 2D nanomaterials: an in-situ microscopy and spectroscopy study

Host Surface Structure and Reactivity at the Atomic Scale group, Istituto Officina dei Materiali of the Italian National Research Council, Trieste



STM images and models of graphene with substitutional Ni (a) and B (b) atoms.

The synthesis of stable tailored 2D nanostructured systems has become of paramount importance in catalysis, energy conversion and sensing applications. For instance, the functionalization of low dimensional materials, *i.e.*, through substitutional atoms or adatoms (see the figure), may result in an increased chemical reactivity, offering a valid alternative to conventional catalysts. Among the surface sensitive techniques, scanning tunneling microscopy (STM) has the potential to explore the structural and electronic properties of (functionalized) 2D nanostructured materials, offering real-space imaging with atomic scale resolution. When combined with photoemission spectroscopies, owning chemical and reciprocal space sensitivity, within the same (or a UHV-connected) experimental setup, a full in-situ material characterization is possible.

This project will focus on the synthesis of functionalized 2D nanostructured systems, and their characterization through STM and photoemission spectroscopies, providing proof of their enhanced physical and chemical properties. The experimental activity will be based on the expertise of the hosting research group. In particular, the project will rely on the complementarity between a "low temperature" and a "variable temperature" STM, LT- and VT-STM, respectively. In the study of the structural and electronic properties of the synthetized nanomaterials, as well as of their reactivity upon exposure to selected gases, LT-STM will allow cryogenic measurements, down to 4.2K, while VT-STM will complement the low temperature data with video-rate imaging, in realistic thermodynamic conditions, and in a temperature range up to 900 K. The use of XPS/UPS to characterize chemical properties, and LEEM/PEEM to access electronic structure and surface composition, will complement the microscopy data. Furthermore, the upgrade of the sample hosting plates and sample holders of both LT- and VT-STM will guarantee a full exchangeability of samples among LT-STM, VT-STM, XPS/UPS and LEEM/PEEM, preventing detrimental exposition of the material to the air.

The experimental results will be supported by ab-initio calculations performed through external collaborations. Beamtime application to external synchrotron radiation facilities will also be encouraged and supported.

The ideal PhD candidate is expected to have a Master degree in Physics, Chemistry or Materials Science, previous experience with vacuum technology and surface science techniques, high drive to solve challenges independently, attitude to work in an international research environment with collaboration spirit, and good English skills. Skills in scripting and analysis using programming languages as well as in the building/maintenance of experimental setups will be added values.

# References

https://www.iom.cnr.it/research-facilities/facilities-labs/analytical-microscopy-and-spectroscopy/stras/ Chesnyak V. et al. Nanoscale 14 (9), 3589-3598 (2022) 10.1039/D1NR06485A Sala A. et al. Advanced Functional Materials 32 (10), 2105844 (2022) 10.1002/adfm.202105844 Fiori S. et al. Carbon 11(20), 8887-8892 (2020) 10.1016/j.carbon.2020.09.056 Patera L.L. et al. Science, 359-6381:1243-1246 (2018) 10.1126/science.aan8782

SupervisorDr. Cristina AfrichCo-SupervisorDr. Cinzia Di Giorgio

africh@iom.cnr.it digiorgio@iom.cnr.it

# 3D radiation detectors based on engineered quantum semiconductors

Dr. Giorgio Biasiol, Istituto Officina dei Materiali, Consiglio Nazionale delle Ricerche, AREA Science Park Basovizza, Trieste

The study of time-resolved ultrafast phenomena with radiation ranging from the infrared to the hard X-rays will be one of the research fields in frontier science in the coming years. Detectors are an indispensable element for any experiment with photon sources. Research in detectors is therefore continuously stimulated by increasingly stringent requirements, both on the source side and on the experimental needs one. Among the aspects that need to be improved are quantum efficiency, which is very poor for silicon-based detectors in the case of hard X-rays, and temporal resolution.

This project aims to develop single-photon detectors that cover frequencies ranging from the infrared to the hard X-rays with 3D (x-y-time) resolution. Avalanche photodiodes with separate absorption and multiplication regions (SAM-APD), based on III-As semiconductors, will be used (right) [1]. Thanks to the higher atomic number they are considerably more efficient and faster than silicon in absorbing hard X-rays and possibly pushing the temporal resolution in the range of 10 ps. The activity carried out so far has allowed the demonstration and optimization of prototypes of





SAM-APD with state-of-the-art performance for absorption, response speed and signal-to-noise ratio (left) [2]. Starting from these results, the project aims to develop single-photon multiband detectors with unprecedented spatio-temporal resolution by improving the structures already made, and applying local functionalizations with ion beams and hard X-ray irradiation.

The involvement of research centers in the definition of the training path also in the context of broader collaborations with the University will be one of the strengths of this doctoral proposal, as

detailed below. These collaborations will ensure that the PhD student can take advantage of qualified and specific operational and scientific structures for study and research activities.

Low-dimensional, band-engineered quantum structures will be synthesized by molecular beam epitaxy and lithographically fabricated by the student at CNR-IOM in Trieste. Spatial resolution at the sub-µm scale will be achieved by local functionalization by ion beam implantation through an electrostatic accelerator, which allows the localized alteration of the quantum mechanical properties of matter, at the Legnaro National Laboratories of INFN. A collaboration with Elettra-Sincrotrone Trieste and the University of Trieste, besides the development of measurement electronics, will allow the student to measure the device performance in terms of gain, noise and time response both with conventional and synchrotron radiation light sources. The activities will also be carried out in close collaboration with the Department of Engineering of the University of Udine, which will provide theoretical modeling of the devices. Finally, the student will benefit from a collaboration with the CNR-IOM LISA beamline at ESRF Grenoble, capable of generating bunches of beams lasting a few tens of ps and energies up to 90 keV (not reachable at Elettra).

# References:

[1] J. Lauter et al 1995 NIMPR A 356 324, DOI: 10.1016/0168-9002(94)01237-7

[2] C. Nichetti et al 2020 JINST 15 C02013, DOI: 10.1088/1748-0221/15/02/C02013

# NANOTECHNOLOGY PhD program @ UniTS Exploring the *nano-bio interface* with SERS spectroscopy Biofluids on metal nanostructures

Prof. Alois Bonifacio – abonifacio@units.it – https://orcid.org/0000-0002-2251-7786



A better understanding of the interaction between metal nanostructures, such as metal nanoparticles, and biological fluids (e.g. serum, urine, saliva) is a necessary step toward the **application of nanotechnology to biological systems**, and in particular to humans. **Gold and silver nanoparticles**, as well as 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.

In this project between nanotechnology and photonics, 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 to characterize the nanostructures and the nanobio interface, also in collaboration with other centers, such as electron microscopy (TEM, SEM), Dynamic Light Scattering (DLS), fluorescence, and FT-IR among others. Raman spectroscopy will be extensively used, also using Raman microscopes to get images. While studying the nano-bio interface, candidates will be also encouraged to explore and develop possible bioanalytical or clinical applications relying on their findings. Candidates will also have the chance to learn and apply advanced data analytics (including machine learning) to fully exploit the information present in their spectroscopic datasets.

**KEYWORDS**: metal nanoparticles, nanostructured metal surfaces, surface enhanced Raman scattering, SERS, metabolomics, nano-bio interface, bioanalytical spectroscopy

#### **KEY PUBLICATIONS**

Biomedical SERS-the current state and future trends, 2024, Chemical Society Reviews, 53, 8957-8979

<u>Label-free surface-enhanced Raman spectroscopy of biofluids: fundamental aspects and diagnostic applications</u>, 2015 Analytical and bioanalytical chemistry 407, 8265-8277

Direct comparison of different protocols to obtain surface enhanced Raman spectra of human serum, 2024, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 317, 124390

# 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 techniques<sup>1</sup>. 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 methods<sup>2</sup>. In a recent paper it has been shown that when deposited on glass substates 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 characterization<sup>3</sup>. 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.

References

- 1. F. Perissinotto et al. Nanoscale 13 5224 (2021)
- 2. E. Sezgin et al. Nat. Protoc. 7 1042 (2012)
- 3. S.-W. Lyu et al., Sci. Rep. 9, 2747 (2019)

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

## Project title: Thermodynamic non-equilibrium probes of cells metabolism

## Supervisors: Dan Cojoc, (CNR-IOM cojoc@iom.cnr.it ) and Edgar Roldan, (ICTP-QLS, edgar@ictp.it )

Cell metabolism is crucial for life because it's the set of chemical reactions that enable cells to obtain energy from nutrients and build the necessary structures for survival and reproduction. Dysregulation of metabolism is implicated in various diseases, including diabetes, cancer, and other metabolic disorders, therefore understanding how cellular metabolism is affected in disease states is crucial for developing new therapies.

Characterizing the thermodynamic properties intrinsic to life is among the central goals of current theoretical and experimental research in nonequilibrium statistical physics, active matter, nanotechnology and biophysics. Over the last decade, researchers have developed accurate numerical schemes to quantify nonequilibrium properties of small biological systems as living cells in several experiments, opening new avenues for applications of the emerging field of stochastic thermodynamics in a broad biological context. However, quantifying *in concert* heat, work and information fluxes in living cells is a research direction still to be explored.

Over the last few years, membrane fluctuations of living red blood cells (RBCs) have been established as a paradigmatic case study of nonequilibrium fluctuations in cells. Stochastic-thermodynamics concepts applied to optical-microscopy experiments have suggested that the entropy flow along the RBC membrane equatorial cell contour is spatially heterogeneous, with correlation lengths of about a micron. However, it remains unclear, for example, whether RBCs dissipate more heat around their central region (where the cell is more rigid and contains most of its hemoglobin) or around their peripheral region (where the membrane is more flexible).

In this project, we will combine optical tweezers microscopy **experiments** with stochastic thermodynamics **theory** by joining together the expertise of two leading groups in optical tweezers (Cojoc) and statistical thermodynamics (Roldan), both based in Trieste.



Schematic of a dual-trap (beads B1 B2) experiment which allows access to thermodynamic fluxes (heat Q, work W, information I) in the vicinity of a cell membrane, resulting from their nonequilibrium activity.

### Key goals of the project:

(1) establish theoretical estimates for how the heat dissipation across RBC stochastic models depends on their local mechanical (e.g. friction) and chemical (e.g. active temperature) properties;

(2) perform dual-trap experiments with optically-trapped colloidal particles near the RBC membranes under different levels of activity (see Figure at the left);

(3) analyze the experimental data in the light of stochastic thermodynamics in order to access heat and information flows between the beads that are intrinsic to RBC's inhomogeneous activity;

(4) extend this approach to cancer cells characterization.

# Direct thin liquid sheet XUV spectroscopy

Supervision: Dr. M. Coreno, Dr. R. Mincigrucci, and Prof. A. Morgante https://web.units.it/dottorato/nanotecnologie/en/node/5045 e-mail : marcello.coreno@cnr.it

Most of the chemical reactions of technological [1] and biological relevance [2] happens in liquid environments. While for some photoinduced processes in solution, knowledge of the gas phase reactivity can be very informative, for others, the environment plays a key role in determining reaction outcomes [3].

Despite their tremendous importance severe technological hurdles hinder studies of the liquid phase in the XUV photon energy range, where photons are strongly absorbed in few hundreds of nm by any solid/liquid material, and gas pressures close to the atmospheric ones causes the total extinction of the XUV beam in few micron [4].

A recent development in microfluidic chips [5] showed that gas jets can squeeze a cylindrical liquid jet thicknesses down to tens of ns, while appropriate pumps are keeping the chamber pressure in the 10<sup>-3</sup> limit. A collaboration between the LDM research group and the EIS group at FERMI has recently replicated these achievements in an UHV chamber obtaining sheets similar to those in the literature (fig. 1). It is now necessary to demonstrate that reproducibility and stability of minimum thickness of nanosheet liquid jets, to allow stable conditions for experimental investigations at synchrotron and FEL.

The PhD project will focus on the characterization of liquid jets to attain stable condition for investigation of pure solvents (water, ethanol, ...) and solutions by means of XUV absorption and photon in - photon out techniques. These results will establish the feasibility of NEXAFS and XES measurements on aqueous and organic solutions relevant to nanotechnological research, such as iron III / IV redox systems, and organic radicals used in CO<sub>2</sub> recapture processes. XUV spectroscopies will be exploited to study modifications of their electronic structure induced by solute-solvent interaction, whereas their relaxation dynamics are going to be probed by pump-probe techniques with laser, synchrotron and FEL radiation.



Fig. 1 : Image of the liquid sheet obtained at Elettra.

Fig. 2 : Microfluidic nozzle.

Fig. 3 : Image of the parylene film separating the liquid jet chamber  $(10^{-3} \text{ mbar})$  from the high vacuum environment  $(10^{-6} \text{ mbar})$  for XUV spectroscopies.

- [1] S. Ha et al., Chem. Sci. 8 (2017) 2522 . DOI: 10.1039/C6SC04474C
- [2] R. Kohen et al., Toxicologic Pathology **30** (2002) 620. DOI: 10.1080/01926230290166724.
- [3] S.J. Harris, et al. PCCP **15** (2013) 6567. DOI: 10.1039/c3cp50756d
- [4] see https://henke.lbl.gov/optical\_constants/
- [5] J. Koralek et al., Nature Communications 9 (2018) art. n. 133. DOI: 10.1038/s41467-018-03696-w|

# **Nanodiamonds in Theranostics**

**Supervisor**: Tatiana Da Ros email: daros@units.it

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 a sp<sup>3</sup> diamond core and their surface is generally present a mixture of sp<sup>2</sup> and sp<sup>3</sup> 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.<sup>1</sup> 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).<sup>2</sup> 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.<sup>3</sup> 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<sup>4</sup> 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<sup>5</sup> and in this respect various derivatization methodologies will be optimized and dedicate to the preparation of derivatives with theranostic applications.

### **References:**

- 1. V. N. Mochalin, O. Shenderova, D. Ho, Y. Gogotsi; Nat Nanotechnol 2011, 7 (1), 11-23.
- 2. A. M. Schrand, S. A. C. Hens, O. A. Shenderova; *Crit Rev Solid State Mater Sci* **2009**, *34* (1-2), 18-74.
- 3. O. Shenderova, A. Vargas, S. Turner, D. M. Ivanov, M. G. Ivanov; *Tribology Transac* **2014**, 57 (6), 1051-1057.
- 4. A. Krueger; J Mater Chem 2008, 18 (13), 1485-1492.
- 5. L. Fusco, E. Avitabile, V. Armuzza, M. Orecchioni, A. Istif, D. Bedognetti, T. Da Ros, L. Delogu; *Carbon*, **2020**, *160*, 390-404.

#### ON-SURFACE MODIFICATION OF ORGANIC SEMICONDUCTORS (OSMOS)

Study of the synthesis and modification of molecules on metals and metal oxides in UHV environment with the aim of improving the charge transport properties at the interface and/or enhancing the catalytic properties of the reaction products. The research activity is performed at Sincrotrone-Elettra in the OSMOS lab and ALOISA (https://www.elettra.eu/elettra-beamlines/aloisa.html) beamline.

#### **RESEARCH LINES**

<u>*RL1*</u>: Morphological and structural characterization of self assembled layers of organic molecules, namely polyconjugated and heteroaromatic compounds (oligomers, polyacenes, perylenes, porphyrins and their derivatives). Study of the charge transfer and molecular bonding to the substrate, the on-surface molecular modifications, as well as the chemical interactions and linking in hetero-molecular systems, both in 2D and 2D+1 architectures.

<u>*RL2*</u>: Synthesis of 2D frameworks on surfaces, using small molecular precursors, aimed at modifying the chemical and morphological properties of the substrate. The main goal is to build 2D templates with specific chemical properties, able to selectively anchor guest species via molecular recognition.



LEFT: bowl-shaped corannulene molecules are trapped inside an artificially created triangular hole (8 nm side) on Ag(111); the fading intensity of the molecules on the upper terrace originates from the decrease of residence time due to molecular mobility. RIGHT: the pathway to 2D boronic condensation on Au(111) of naphtalene boronic acid through intermediate precursor stages: paired monomers at 250 K, partially condensed paired dimers at 300 K, and fully condensed trimers at 350 K.

#### EQUIPMENT

- The OSMOS laboratory for microscopy (joint project between CNR-IOM and Sincrotrone-Elettra) is composed of three interconnected experimental chambers, including i) variable temperature STM chamber (SPECS Aahrus), ii) sample preparation chamber equipped with LEED and quartz microbalance, iii) X-ray spectroscopy chamber equipped with an Al/Mg X-ray source PSP Tx-400 and a monochromatized Gamma Data VUV 5k source (He I, II), which are coupled to a Scienta R3000 (150mm) electron spectrometer with CCD detector, and a closed-circuit liquid He cryostat (11 K on sample) for in-situ XPS and angle-resolved UPS analysis.

- The project takes advantage of direct access to the Synchrotron beamline ALOISA (responsible Luca Floreano) for performing high resolution fast-photoemission, resonant photoemission and X-ray absorption spectroscopy (NEXAFS) at variable scattering and polarization geometries.

#### CONTACTS

Luca Floreano CNR-IOM floreano@iom.cnr.it

Andrea Goldoni Elettra-Sincrotrone Trieste andrea.goldoni@elettra.eu

# 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 email: pfornasiero@units.it

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.<sup>[1]</sup> 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.<sup>[2]</sup> 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 metalfree 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 photocalysts for organic synthesis

# **References:**

- [1] I. Ghosh, J. Khamrai, A. Savateev, N. Shlapakov, M. Antonietti, B. König, *Science* **2019**, *365*, 360-366.
- G. Filippini, F. Longobardo, L. Forster, A. Criado, G. Di Carmine, L. Nasi, C. D'Agostino, M. Melchionna, P. Fornasiero, M. Prato, *Science Advances* 2020, *6*, eabc9923.

## NANOSTRUCTURED BIOMATERIALS for MEDICINE

#### Supervisor: Prof. S. Marchesan <u>www.marchesalab.com</u>

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.<sup>1</sup> 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.<sup>2,3</sup> They are particularly attractive to reconstruct conductive tissues, such as the heart<sup>4</sup> and the nerve tissue,<sup>5</sup> but are also convenient scaffolds for advanced diagnostics, for instance for cancer detection.<sup>6</sup> 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.<sup>7</sup> In particular, self-assembling short peptides are very interesting building blocks that not only can yield biocompatible hydrogels,<sup>8-10</sup> but can also interact favourable with carbon nanostructures, which can add further properties, such as self-healing behaviour.<sup>11</sup>

Research in this hot area will involve the functionalization and characterization of nanocarbons and their conjugation with short self-assembling peptides and other biolomolecules 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.



S. Marchesan, et al. ACS Med. Chem. Lett. 2013, 4, 147. 2. S. Marchesan, et al. Chem. Commun. 2015, 51, 4347. 3. A. Criado, et al., angew. Chem. Int. Ed. 2015, 54, 10734. 4. S. Marchesan, et al. Nano Today 2016, 11, 398. 5. S. Marchesan, et al. Science 2017, 356, 1010. 6. S. Piovesana, et al., Nano Res. 2020, 13, 380. 7. D. Iglesias, et al., Curr. Top. Med. Chem. 2016, 16, 1976. 8. A. M. Garcia, et al. Chem 2018, 4, 1862. 9. S. Kralj, et al. ACS Nano 2020, 14, 16951. 10. A. M. Garcia, et al. ACS Nano 2021, 15, 3015. 11. D. Iglesias, et al. ACS Nano 2018, 12, 5530.

# Photothermal heterogenous catalysts for energy-related applications

Supervisor: Prof. Tiziano Montini (University of Trieste), tmontini@untis.it

Co-supervisor: Prof. Paolo Fornasiero (University of Trieste), Prof. Alberto Naldoni (University of Turin).

Concentrated solar power (CSP) enables storing energy in high-temperature heat, which later can be converted to electricity. While such technology is already commercially available, a similar architecture has been explored to produce fuels (such as CO, CH<sub>4</sub> or H<sub>2</sub>) using thermochemical pathways. Recent studies have demonstrated the generation of fuels or chemicals under moderate concentration regimes by exploiting catalysts including plasmonic nanoparticles. The latter can significantly alter the reaction mechanisms and, therefore, product selectivity by means of nonthermal plasmonic effects, which occur simultaneously with purely thermal ones, making sustainable an energy-demanding production process.

In this project, TiN plasmonic nanostructures will be decorated with metal nanoparticles by sputtering or wet impregnation. Both monometallic or bimetallic systems will be investigated, to investigate the role of metal-metal interaction on the catalytic activity. For specific applications, TiN plasmonic materials will be covered with an oxidic layer by ALD before metal nanoparticles deposition (i.e. Al<sub>2</sub>O<sub>3</sub> as inert layer to discriminate thermal and electronic activation of the catalytic metal nanoparticles; CeO<sub>2</sub> or Fe<sub>2</sub>O<sub>3</sub> as redox promoter in the formulation of the photocatalysts). The obtained materials will be employed as heterogeneous catalysts in reactions relevant for sustainable energy production: CO<sub>2</sub> reduction to CO or CH<sub>4</sub> and H<sub>2</sub> production from alcohol reforming (methanol or ethanol). The nanostructure of the active photocatalysts will be investigated in detail by means of state-of-the-art techniques offered by the modern nanotechnology, such as electron microscopy (SEM, TEM), spectroscopy (XPS, XANES/EXAFS, FT-IR) and diffraction (gracing incidence XRD).



#### **Research Topic: Charge transfer process in complex interfaces**

#### Supervision:

Albano Cossaro (Department of Chemical and Pharmaceutical Sciences University of Trieste, CNR-IOM Laboratorio TASC) e-mail: <a href="mailto:cossaro@iom.cnr.it">cossaro@iom.cnr.it</a>

Martina Dell'Angela (CNR-IOM Laboratorio TASC) e-mail: dellangela@iom.cnr.it

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 selfassembled 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.



# DYNAMICS NANOMATERIALS WITH FUNCTIONAL PROPERTIES

## Supervisor: Paola Posocco (University of Trieste)

The research activity will focus on studying self-assembling dynamic nanomaterials in equilibrium and out-of-equilibrium conditions to understand key molecular factors, forces and properties that control self-assembly, structure, reaction, adaptability, and recognition properties. Two main classes will be investigated by computational techniques and machine-learning approaches: peptide-based systems and organo-modified metal nanoparticles. Via the integration of classical atomistic and coarse-grained molecular simulations, advanced molecular simulation methodologies and data-driven models, the candidate will explore structure, dynamic and functional behavior of these fascinating nanomaterials on a wide spatio-temporal scale. The activity will be carried out in collaboration with national and international experimental groups. The research project can be adapted and tailored based on the candidate developing skills, interests, and the results achieved throughout the course of the research.

The ideal candidate has a Master Degree in Chemistry, Physics or Materials Science. Basic experience with common molecular simulation packages (e.g. LAMMPS, GROMACS, AMBER) is required, along with reasonable programming skills (Python or Fortran). Strong motivation and enthusiasm for research, good attitude to work in team, good written and spoken English is also an asset.

# REFERENCES

- Kravets, M. et al., Pursuing the Complete OFF State in Photoswitchable Catalysis ACS Catal. 2023, 13, 24, 15967.
- o Hyziuk, P. et al., Creating a suprazyme: integrating a molecular enzyme mimic with a nanozyme for enhanced catalysis *Chem. Sci.*, **2024**, 15, 16484.
- o Gabellini, C. et al.; Spotting Local Environments in Self-Assembled Monolayer-Protected Gold Nanoparticles, *ACS Nano* **2022**, 16, 20902.
- Mati, I. K. et al.; Probing Multiscale Factors Affecting the Reactivity of Nanoparticle-Bound Molecules. ACS Nano 2021, 15, 8295.
- o Sheehan, F. et al.; Peptide-Based Supramolecular Systems Chemistry. *Chem. Rev.* 2021, 121, 13869.
- Luo, Z. et al.; Quantitative 3D Determination of Self-Assembled Structures on Nanoparticles Using Small Angle Neutron Scattering. *Nat. Commun.* 2018, 9, 1343.
- Sologan, M. et al.; Patchy and Janus Nanoparticles by Self-Organization of Mixtures of Fluorinated and Hydrogenated Alkanethiolates on the Surface of a Gold Core. ACS Nano 2016, 10, 9316.

## **Contact Details**

Paola Posocco SupraMolecular nAnomaterials computational Lab <u>(SMALL Lab)</u> Department of Engineering and Architecture University of Trieste Marchitecture paola.posocco@dia.units.it