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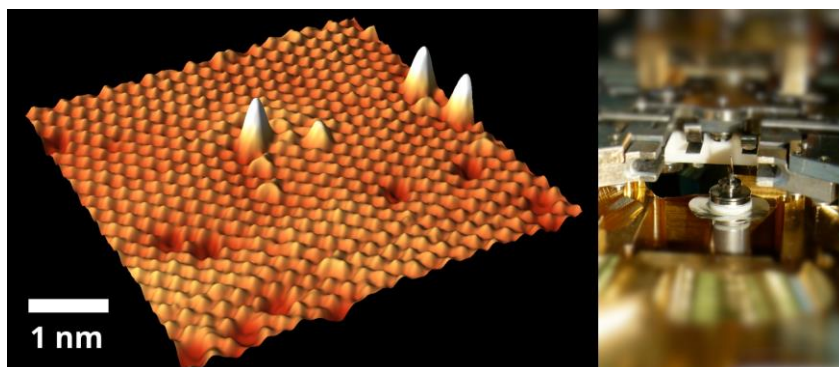
Candidates applying for M/1 and M/2 scholarship may carry out their activity in any of the research groups active within the PhD program in Nanotechnology.

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. 2023/2024.

There are also specific research projects available for candidates applying for M/1 and M/2 scholarship. These are presented in the following pages.

Atomic scale characterization of functionalized 2D materials by scanning tunneling microscopy

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



The synthesis of stable tailored 2D nanostructured systems have become of paramount importance in catalysis, energy conversion and sensing applications. For example, the functionalization of low dimensional materials, resulting in an increased chemical reactivity, offers an alternative route to conventional catalytic processes. In the same way, the development of technologies to convert solar energy into chemical energy and electric power can constitute a valid and green alternative to the technology based on fossil fuels.

This project aims at identifying reproducible and scalable routes towards the synthesis of stable, functionalized 2D nanostructured systems and at providing proof of their enhanced physical and chemical properties. The experimental activity will be based on the expertise of the hosting research group, which exploits Scanning Tunneling Microscopy (STM) to achieve an accurate characterization of the prepared nanostructures. In particular, the project can rely on Low Temperature STM (down to 4 K) to elucidate the atomic structure of the layers and their electronic properties, and on Variable Temperature STM (100-900 K) to investigate at video rate the chemical reactivity over exposure to selected gases in realistic thermodynamic conditions. STM results will be complemented by X-ray photoemission spectroscopy measurement and ab-initio calculations performed through external collaborations. Beamtime application to external synchrotron radiation facilities will be also 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 will be an added value.

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) doi:10.1039/D1NR06485A

Sala A. et al. *Advanced Functional Materials* 32 (10), 2105844 (2022) doi:10.1002/adfm.202105844

Fiori S. et al. *Carbon* 11(20), 8887-8892 (2020) doi:10.1016/j.carbon.2020.09.056

Patera L.L. et al. *Science*, 359-6381:1243-1246 (2018) doi:10.1126/science.aan8782

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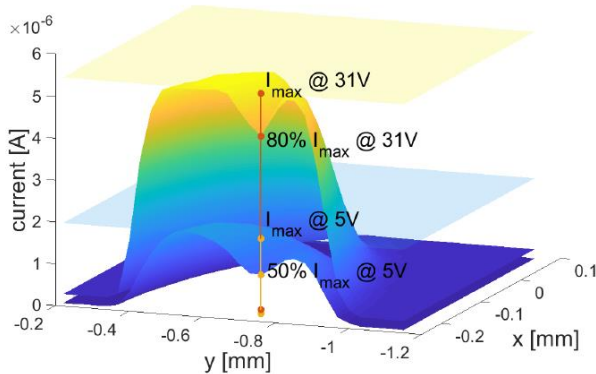
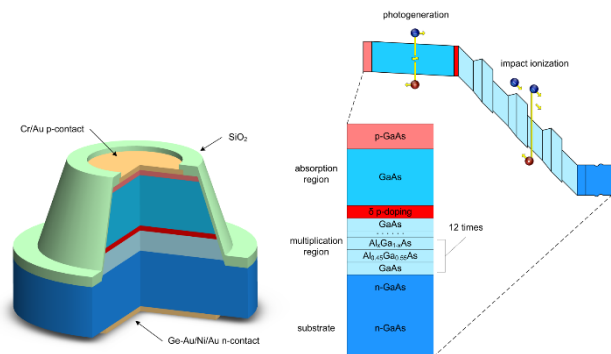
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3D radiation detectors based on engineered quantum semiconductors

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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).

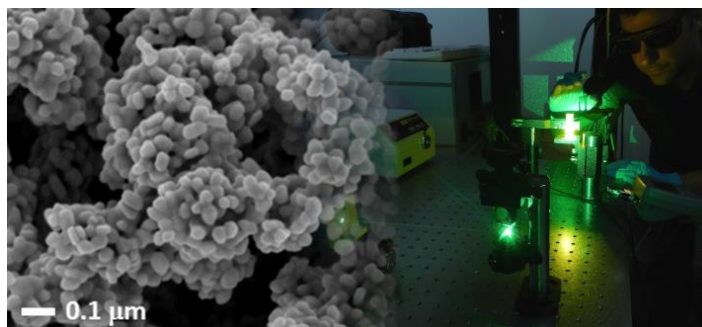
References:

[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

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 these 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

Bonifacio, A., Dalla Marta, S., Spizzo, R., Cervo, S., Steffan, A., Colombatti, A., Sergio, V. *Surface-enhanced Raman spectroscopy of blood plasma and serum using Ag and Au nanoparticles: A systematic study* (2014) *Analytical and Bioanalytical Chemistry*, 406 (9-10), pp. 2355-2365.

Bonifacio, A., Cervo, S., Sergio, V. *Label-free surface-enhanced Raman spectroscopy of biofluids: Fundamental aspects and diagnostic applications* (2015) *Analytical and Bioanalytical Chemistry*, 407 (27), pp. 8265-8277.

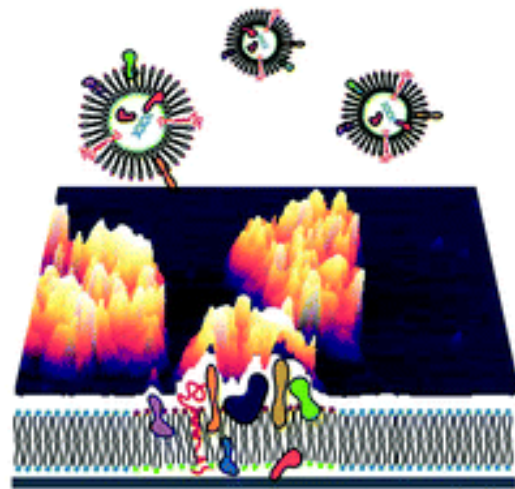
Genova, E., Pelin, M., Decorti, G., Stocco, G., Sergio, V., Ventura, A., Bonifacio, A., *SERS of cells: What can we learn from cell lysates?* (2018) *Analytica Chimica Acta*, 1005, pp. 93-100.

Fornasaro S., Bonifacio A., Marangon E., Buzzo M., Toffoli G., Rindzevicius T., Schmidt M.S., Sergio V., *Label-free quantification of anticancer drug imatinib in human plasma with surface enhanced Raman spectroscopy* (2018) *Analytical Chemistry*, 90, pp. 12670-12677.

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.

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

Direct thin liquid sheet XUV spectroscopy

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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^{-3} 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 CO₂ 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.

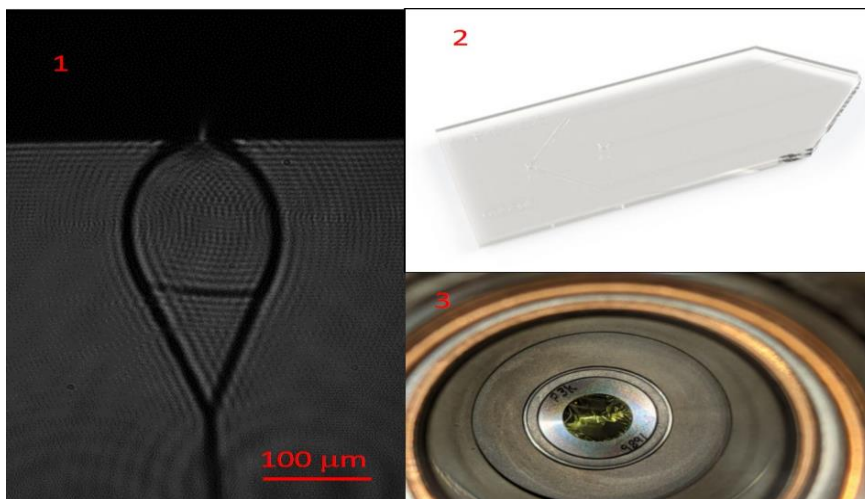


Fig. 1 : Image of the liquid sheet obtained at Elettra.

Fig. 2 : Microfluidic nozzle.

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

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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 quite recent, with the development of nanotechnology. They have a 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 methods⁴ 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 purposes⁵ and in this respect various derivatization methodologies will be optimized and dedicated 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.

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.

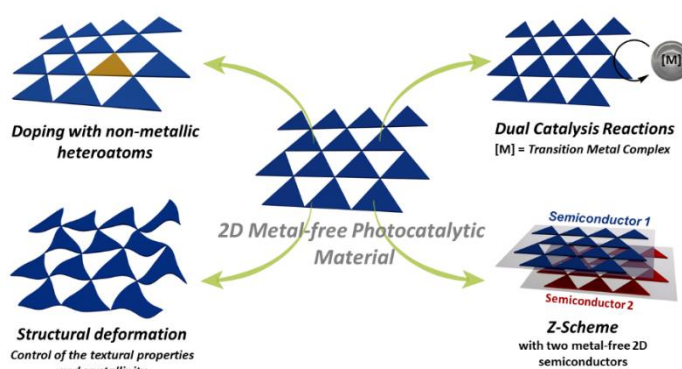


Figure 1. Envisioned avenues for the development of metal-free photocatalysts for organic synthesis

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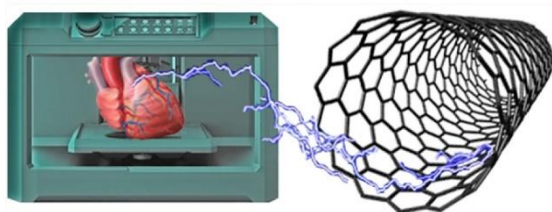
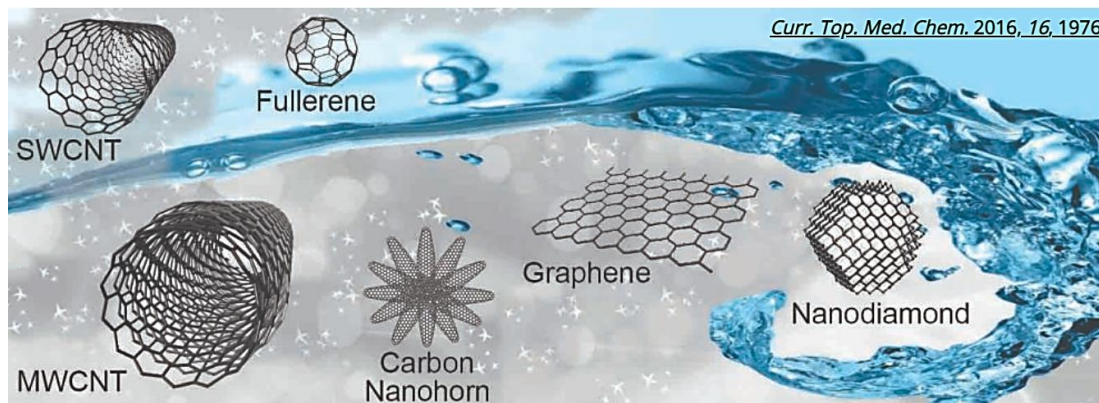
- [1] I. Ghosh, J. Khamrai, A. Savateev, N. Shlapakov, M. Antonietti, B. König, *Science* **2019**, 365, 360-366.
- [2] G. Filippini, F. Longobardo, L. Forster, A. Criado, G. Di Carmine, L. Nasi, C. D'Agostino, M. Melchionna, P. Fornasiero, M. Prato, *Science Advances* **2020**, 6, eabc9923.

NANOSTRUCTURED BIOMATERIALS for MEDICINE

Supervisor: Prof. S. Marchesan 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.



References:

1. 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.

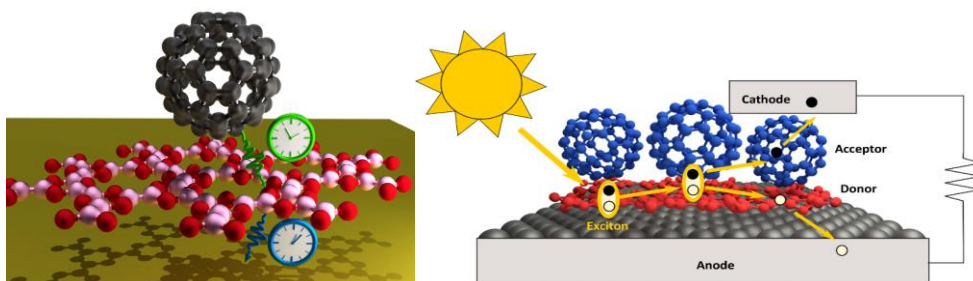
Research Topic: Charge transfer process in complex interfaces

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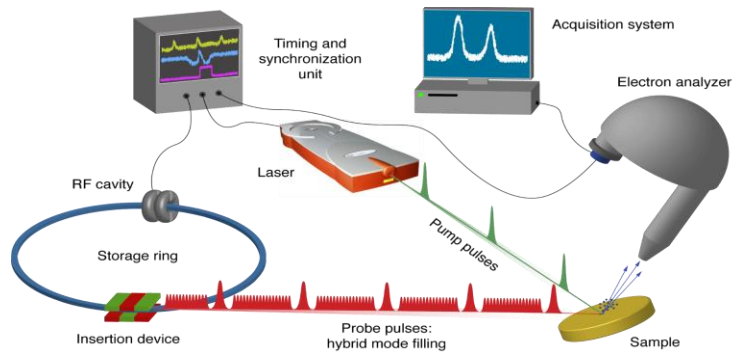
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There is a dramatic raise in the scientific and technological interest for new complex 2D materials that extend substantially the graphene family (2D dichalcogenides, phosphorene, hexagonal boron nitride hBN etc), their combination in stacked heterostructures, 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.



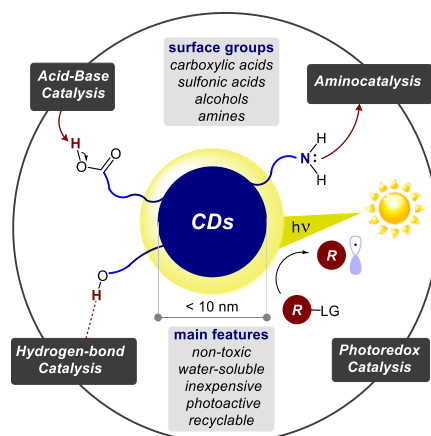
Use of Carbon Dots as Nanocatalysts for Synthetic Applications

Supervisor: Prof. Maurizio Prato (prato@units.it)

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This project aims at producing novel Carbon Dots to use them as nanocatalytic systems for the development of valuable organic transformations.

Carbon Dots (CDs) are an emerging class of quasi-spherical carbon-based nanoparticles with dimensions below 10 nm.^[1] In recent years, CDs have gained popularity thanks to their excellent luminescence and optical features, considerable solubility in aqueous and polar solvents, high chemical and photostability, as well as low toxicity and excellent biocompatibility. These properties have generated a broad research interest that spans over various fields such as chemistry, materials science, biology and medicine. Among these areas of application of CDs, an emerging development is their use as green organocatalysts (Figure 1).^[2] With this in mind, our group demonstrated that amine-rich CDs, produced from arginine and ethylenediamine, can serve as nano-aminocatalysts to drive the functionalization of a variety of sterically hindered carbonyl compounds through enamine or iminium ion activations.^[3]



Carbon dots as nanocatalyst: CDs application in nano-organocatalysis and photocatalysis.

Our objective is to develop novel CDs-based organocatalysts capable of driving valuable synthetic transformations. Thus, this project involves the design and synthesis of new CDs bearing reactive surface groups such as carboxylic acids, sulfonic acids, alcohols, and amines. These functional groups will be employed to catalyse the derivatisation of numerous organic compounds. In this way, the PhD student will become fluent in organic synthesis, catalysis and materials science. The produced nanomaterials will be diligently and comprehensively characterised using state-of-the-art spectroscopic and microscopic techniques. The PhD work will start from an ongoing project. Then, the individual interests and attitudes of the student will come into play and shape the development of her/his path into research.

References:

- [1] “Design, Synthesis, and Functionalization Strategies of Tailored Carbon Nanodots”, F. Arcudi, L. Đorđević, M. Prato, *Acc. Chem. Res.* **2019**, *52*, 2070-2079.
- [2] “Carbon Dots as Nano-Organocatalysts for Synthetic Applications”, C. Rosso, G. Filippini, M. Prato, *ACS Catal.* **2020**, *10*, 8090-8105.
- [3] (a) “Mapping the Surface Groups of Amine-Rich Carbon Dots Enables Covalent Catalysis in Aqueous Media”, G. Filippini, F. Amato, C. Rosso, G. Ragazzon, A. Vega-Peñaloza, X. Companyó, M. Bonchio, M. Prato, *Chem.* **2020**, *6*, 3022-3037. (b) “Use of Nitrogen-Doped Carbon Nanodots for the Photocatalytic Fluoroalkylation of Organic Compounds”, C. Rosso, G. Filippini, M. Prato, *Chem.-Eur. J.*, **2019**, *25*, 16032-16036.

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 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 skill (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

- Mati, I. K. et al.; Probing Multiscale Factors Affecting the Reactivity of Nanoparticle-Bound Molecules. *ACS Nano* **2021**, 15, 8295.
- 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.
- Şologan, 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.
- Monego, D. et al; When Like Destabilizes Like: Inverted Solvent Effects in Apolar Nanoparticle Dispersions. *ACS Nano* **2020**, 14, 5, 5278.
- Marson, D. et al.; Molecular Features for Probing Small Amphiphilic Molecules with Self-Assembled Monolayer Protected Nanoparticles. *Langmuir* **2020**, 36, 20, 5671.

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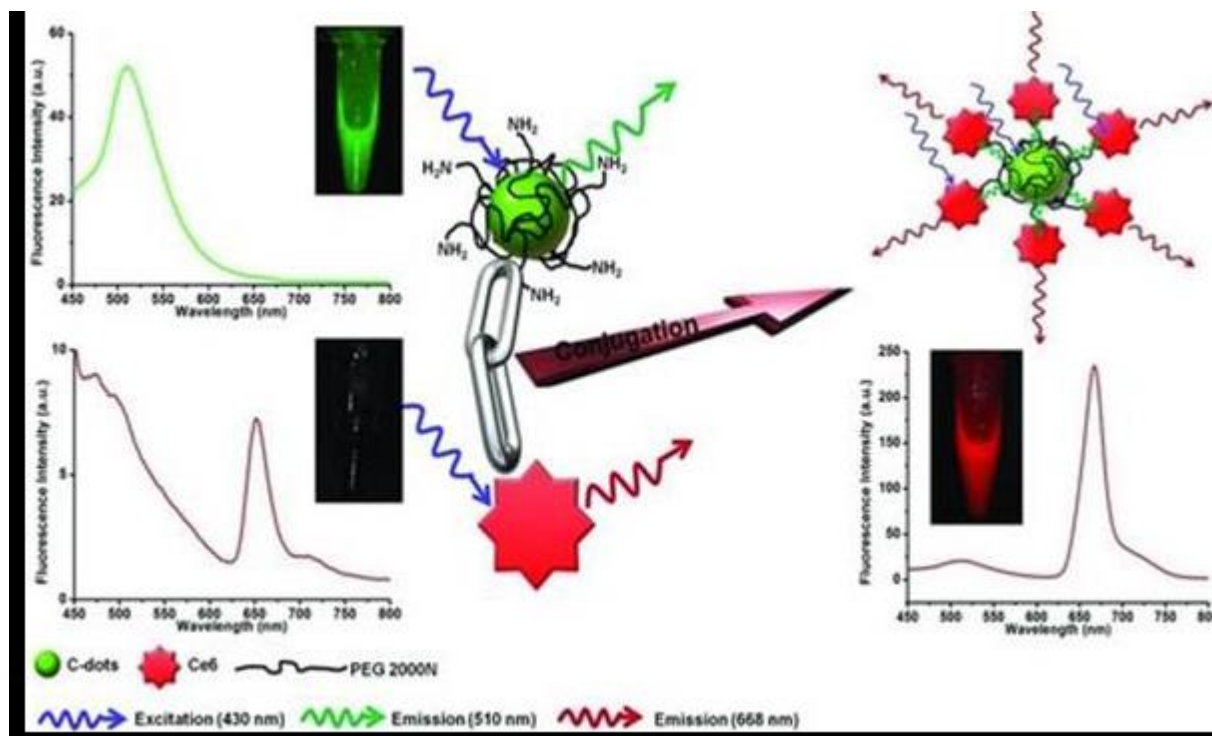
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Anti-Glypican-1 carbon-nanodots for theranostics in pancreatic ductal adenocarcinoma

Pancreatic ductal adenocarcinoma (PDAC) is the most common cancer of the pancreas and it causes more than 330,000 deaths every year worldwide (Rahib L et al. *Cancer Res.* 2014; Ilic M et al. *World J. Gastroenterol.* 2016). In the majority of the cases the diagnosis occurs in an advanced stage where the disease is already spreads in different organs. In this context, surgery is not applicable and chemotherapy is slightly efficient causing severe toxicity to healthy tissues, for these reasons there is an urgent need of new therapeutic strategies (Garrido-Laguna et al. *Nat. Rev. Clin. Oncol.* 2015; Adamska et al. *Int. J. Mol. Sci.* 2017). Glypican 1 (GPC1) is a cell surface proteoglycan that can be an useful target for active drug-delivering in the PDAC context due to its high expression in PDAC cells and its low/absent expression in most other tissues (Kleeff J. et al. *J. Clin. Invest.* 1998; Lu H et al. *Cancer Med.* 2017). Carbon-nanodots (CNDTs) conjugated with molecules that recognize tumor cell targets represent innovative tools both in the therapeutic field for targeted treatments and in the diagnostic field for "imaging". The use of CNDTs in oncology therefore represents a promising theranostic tool (Zhu, C et al. *Chem. Commun.* 2012). The aim of the project is to investigate the theranostic utility of CNDTs conjugated with antibodies the surface tumor associated antigen GPC1 selectively expressed in PDAC. Activities will be carried out to perform the analysis of the chemical-physical characteristics of antibody-conjugated CNDTs, the evaluation of the interaction of functionalized CNDTs with antibodies with selective targets of the GPC1-expressing neoplastic cells, the biodistribution of antibody-conjugated CNDTs in animal models and pharmacokinetics, the evaluation of the in-vitro and in-vivo cytotoxicity of antibody-conjugated CNDTs and of their diagnostic potential in-vivo.



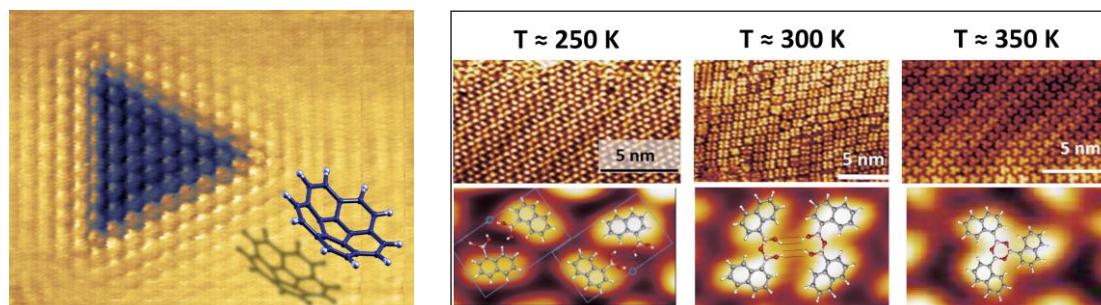
ON-SURFACE MODIFICATION OF ORGANIC SEMICONDUCTORS (OSMOS)

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/aloina.html>) beamline.

RESEARCH LINES

RL1: 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.

RL2: 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 naphthalene 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 Aarhus), 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.

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