

AEROSPACE ENGINEERING / ARCHITECTURAL,  
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MATHEMATICAL MODELS AND METHODS IN  
ENGINEERING / MECHANICAL ENGINEERING  
/ **PHYSICS** / PRESERVATION OF THE  
ARCHITECTURAL HERITAGE / STRUCTURAL,  
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Chairman:  
**Prof. Marco Finazzi**

## DOCTORAL PROGRAM IN PHYSICS

The Doctoral Program in Physics at Politecnico di Milano aims at attracting bright students with good scientific background and clear interest towards development and applications of new ideas and technologies. It offers a wide range of opportunities in the fields of advanced applied physics, such as photonics and optoelectronics (lasers, ultrafast optics), biomedical optics (optical tomography), vacuum technologies (thin film depositions), material technologies (microelectronics and nanotechnologies, micromechanical processing), and advanced instrumentation (electronic and atomic microscopy, nuclear magnetic resonance).

Scientific education and training to develop general research abilities in all areas of applied physics is increasingly needed by advanced technological companies. Through a general education in the basic areas of applied physics and a specific knowledge in condensed matter physics, as well as optics and lasers, the PhD Program aims at the development of an experimental approach to problem solving techniques and at the attainment of a high level of professional qualification.

The Doctoral Program has strongly experimental character. The contents are strictly related to the research activities carried out in the laboratories at the Department of Physics. They can be divided into two main areas:

- a) Condensed Matter Physics, including photoemission; spin-resolved electronic spectroscopy; magneto-optics; X ray diffraction; magnetic nanostructures for spintronics; synchrotron radiation spectroscopy, positron spectroscopy, semiconductor nanostructures.
- b) Photonics and Quantum Electronics, including ultrashort light pulse generation and applications; UV and X optical harmonics generation; biomedical applications of lasers; diagnostics for works of art; laser applications in optical communications; time domain optical spectroscopy and diagnostic techniques.

All research activities rely on advanced experimental laboratories located at Politecnico di Milano (Milano-Leonardo Campus and Como Campus) and are performed in collaboration with several international Institutions. Consistent effort is devoted to experimental research, development of innovative approaches and techniques, and design of novel instrumentation.

The educational program can be divided into three parts: 1) Courses specifically designed for the PhD program as well transdisciplinary courses; 2) Activities pertaining to more specific disciplines which will lay the foundation for the research work to be carried out during the Doctoral Thesis; 3) Doctoral Thesis. The thesis work is the major activity of the Program. It has a marked experimental character and will be carried out in one or more laboratories at the Department of Physics. The students are also encouraged to perform part of their thesis work in

laboratories of other national or foreign Institutions. Collaborations that may involve the PhD students are presently active with several national and international research and academic Institutions, such as: ETH-Zürich, EPL-Lausanne, Lund Institute of Technology, University of Paris-Sud, Ecole Polytechnique-Paris, University of Berkeley, University of Cambridge, University College London, Massachusetts Institute of Technology, Harvard University, European Space Agency, ENEA, Elettra-Ts, PSI-Villigen, Agenzia Spaziale Italiana, European Synchrotron Radiation Facility (ESRF-Grenoble), IFN-CNR, IIT-Istituto Italiano di Tecnologia.

At present, the number of students in the three-year course is 106, and 100 of them have a fellowship.

The PhD Program Faculty, who takes care of organizing and supervising teaching and research activities, consists of members (listed here below), who are all highly qualified and active researchers covering a wide spectrum of research fields. This ensures a continuous updating of the PhD Program and guarantees that the students are involved in innovative research work.

The Doctoral Program relies also on the advice of a Steering Committee, formed by distinguished experts (see table below) coming from R&D industries or research laboratories, who take care that the goals of the PhD Program are in line with the needs of non-academic world.

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\*Position: FP = Full Professor; AP = Associate Professor; ST = Scientist.

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Prof. Hecht	Bert	Universität di Würzburg, D
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Prof. Blandino	Davide	Optec s.p.a.
Prof. Majorana	Salvatore	IIT – Technology Transfer Office

## EFFECTS OF ALKALINE AND SIZING TREATMENTS ON WOOD IN CREMONESE VIOLIN MAKING: CHEMICAL-PHYSICAL CHARACTERISATION AND NEW ANALYTICAL APPROACHES

Michela Albano – Supervisor: Daniela Comelli

Musical instruments have always played a key role in society: they are used to produce sounds for entertainment and ceremonial purposes, encouraging the identification of these objects as vectors of the values of the community to which they belong. For this reason, the musical instrument has a dual nature: the object and the sound. The popularity of the violin family (known as the classic quartet-violin, viola and cello) started in the 16th century. Its fascination is still alive due to its impact on European music for its practice and aesthetics, which reached its apogee with the Cremonese masters. The most renowned families are Stradivari, Amati and Guarneri. Their instruments represent the ideal model for today's makers and the standard that musicians look for. Apart from historical recipe books related to varnishes for furniture, wooden objects or paintings, there are no written sources that explain precisely the materials and practices used by the Cremonese families. In this scenario, driven by the rediscovered value of tradition and the musicians' commitment, the study and characterisation of historical instruments have become a subject of study. Considering the intrinsic chemical and physical nature of the object, scientists began to be engaged in the investigation of such instruments. During the last decades, outstanding results were achieved around the characterization of the complex multi-layered system resulting from the procedures that bring to the finished instrument. They include some unavoidable steps: the chemical pre-treatment of wood, the protein-

based sizing, the ground-coat and a natural resin-based varnish application. A huge variety of organic and inorganic materials can be employed alone or in a mixture, applied in a step of the procedure (a layer) or another one, and can diversely affect the violin properties (aesthetical, chemical, and acoustic). While this aspect seems to be understood, most of the studies deals with the bare wood and the varnish, without taking into account the pre-treatment and sizing, although the first modify the chemistry of the wood and the other change the density of the uppermost part of the wood, probably affecting the mechanical properties. The lack of such knowledge depends on the very little information available for these treatments and the complexity of identifying them in historical samples. In fact, the pre-treatment does not generate a real tangible layer, but it modifies the wood with an effect presumably close to the natural ageing. With this research project, we decided to take up the challenge and focus the attention on the less investigated part of the stratigraphy, trying to clarify its role in the evolution of the wood finish properties. It required to fix double aims: the first related to the chemical property characterization, the latter about the analytical strategy to detect the hidden layers in the historical stratigraphies. Hence, we can concisely describe the aims as follows: (i) examine the effect of the pre-treatments on the wood chemical feature with an insight on the vibromechanical properties; (ii) improve the analytical methodologies based on a spectroscopic approach for the

characterization of the complex multi-layered coating system of historical instruments. About the first issue we focused on the most employed alkaline chemical pre-treatments, e.g., potassium hydroxide aqueous solution and ammonia fuming. In some cases, we also considered their combination with protein-based sizing treatment (i. e., rabbit glue, potassium caseinate and rabbit glue mixed with kaolin). A proper analytical protocol was developed and applied to laboratory mock-ups of treated spruce wood (to simulate the soundboard of violins), to detect the induced chemical and structural changes. The core of the analytical approach is dedicated to the chemical aspect and is based on the use of several complementary analytical methodologies to assess each wood component (hemicellulose, cellulose and lignin) qualitatively and quantitatively. We combined: FTIR Spectroscopy in ATR mode (FTIR-ATR), analytical Pyrolysis coupled with the Gas Chromatography/Mass Spectroscopy Py(HMDS)-GC/MS (where 1,1,1,3,3,3-hexamethyldisilazane - HMDS - was used as a silylation agent) and Gel Permeation Chromatography (GPC), in addition X-Ray Diffraction (XRD) and Scanning Electron Microscopy equipped with the microanalysis probe (SEM-EDX). For aesthetical and morphological characterization colorimetry and optical microscopy under visible light and UV Induced Fluorescence (UVIFL) were used. Furthermore, we estimated the vibrational properties exploiting the dynamic resonance method by comparing the frequency response function (FRF) and extrapolating the

Young's modulus. The most relevant finding consisted in proving the correlation between the chemical transformation carried out by the alkaline pre-treatment on vibrational properties. Particularly, we evidenced the modifications of LCCs (known as responsible for wood mechanical behaviour) coupled to the changes in the vibrational properties. Finally, we demonstrated that the overlapping of materials and layers could lead to a completely different overall effect than the one obtained with the single layer, which incorporates the partial and produces a new one. In this view, investigating the single layer and its relationship to the surrounding layers is of primary importance to understand and address the finished surface of the historical instrument. Concerning the second issue of the project, we proposed to improve the traditional approach by replacing the observation of UV-induced fluorescence under the microscope with the micro-photoluminescence spectroscopy joint to the hyperspectral detection (HS PL micro-imaging). It could provide fluorescence spectra, hence measurable quantities available rather than qualitative information. Integrating this methodology with the traditional micro-FTIR mapping and SEM-EDX, we built up a protocol that allows us to fully characterize the multi-layered coating system of wooden instruments. We believe this improvement is capable to overcome the limitations of UV-induced fluorescence investigation, extending the potentiality of the dataset processing through the multivariate analysis method. Three cross-sectional

samples from three violins made by Lorenzo Storioni at the end of the 18th century in Cremona (Italy) were investigated to test the methodology and a properly laboratory mock-up was used to set the protocol. The complex multi-layered micro-samples were morphologically and chemically characterized even when the layers were a few micrometres thick and overlapped. The study of the samples demonstrated: (i) the specificity of the PL signal for the madder lake detection, (ii) the possibility of obtaining the spatial distribution of layers with micrometre resolution; (iii) the opportunity to disclose and assess the sizing layer features; (iv) the effectiveness of the method for the identification of alteration/restoration layers. In conclusion, we strongly believe that the role of our results in the literature is highly relevant. Today, if the cause of the acoustic quality of the violin could not be attributed to the varnish and the thickness of the soundboard alone, it is now considered true that it probably lies in the wood treatments. Our findings support that hypothesis and represents the first concrete step aimed to prove it. Moreover, they pursue the research of the future driving the focus on the methodologies and the resolution required to investigate hidden layers, furthermore setting the precondition of using an experimental approach to study the effect produced by the single and/or the sum of the layers in the wood finish of musical instruments.

## HYBRID DCS AND TD-NIRS DEVICES FROM DEVELOPMENT THROUGH APPLICATIONS IN INTENSIVE CARE UNIT

Caterina Amendola – Supervisor: Lorenzo Spinelli

Oxygen delivery to metabolically active cells is necessary for adenosine triphosphate (ATP) generation and irreversible tissues impairment could rapidly occur when its transport mechanisms are damaged. Many diseases such as anaemia or acute respiratory distress syndrome (ARDS), could affect the functioning of oxygen delivery, causing localized or generalized hypoxia. The reduced amount of oxygen delivery could be related to both hypoperfusion (small quantity of blood) or hypoxemia (low level of oxygen in the blood). Indeed, the vast majority of oxygen is transported in the blood, bound to haemoglobin within red blood cells (RBCs). In these scenarios, it is paramount to develop techniques that allow for early diagnosis, risk assessment and tailored treatments to each individual. The most appropriate parameters related to effective oxygen transportation are haemoglobin concentration, and oxygen saturation levels. Positron emission tomography (PET), contrast-enhanced magnetic resonance imaging (MRI), and Xenon clearance are the techniques generally used in clinics to assess tissue haemodynamics. However, these approaches are bulky, need patient immobility, and some of them make use of radioactive tracers.

In this scenario, diffuse optics (DO) techniques seem to be perfect candidates, since they allow for non-invasive and continuous monitoring of the oxygenation and perfusion of specific tissues, also at bedside. Among them, Near-Infrared Spectroscopy (NIRS) exploits light in the near-infrared region to investigate chromophore

concentrations and movement. In this range of wavelengths, photons can penetrate for a few cm into the tissue and, then, from their interaction with probed tissue haemodynamic parameters are retrieved. In particular, Time Domain Near-Infrared Spectroscopy (TD-NIRS) enables to retrieve tissues chromophore concentrations (i.e. oxygenated and deoxygenated haemoglobin), while Diffuse Correlation Spectroscopy (DCS) allows to assess the flow of RBC, by assuming their motion as Brownian and measuring the diffusion coefficient (Db). In the past years, the improvements in technology paved the way for the development of portable and user-friendly devices, which can also be exploited in hostile environments such as Intensive Care Unit (ICU) for real-time monitoring of microvasculature health of ill patients.

In this work, TD-NIRS and DCS techniques were investigated and exploited: from one side, we assess TD-NIRS accuracy in estimating neonatal cerebral haemodynamics, and, from the other, we develop and characterize a compact hybrid device that combines TD-NIRS and DCS modules, towards the exploitation of hybrid devices in Intensive Care Unit (ICU).

In particular, two different hybrid DO devices were used to address tissue haemodynamics in two populations: preterm neonates and adults. We interrogate on the accuracy of TD-NIRS homogeneous model in estimating neonatal brain haemodynamics. Indeed, when TD-NIRS is used for monitoring neonatal health it is paramount to assess the ability of

this technique in measuring vital parameters like oxygen saturation and haemoglobin concentration. Thus, Monte Carlo simulations were performed to mimic photons propagation in realistic head structures of preterm and term neonates, and real pathological conditions (i.e. ischemia, hyperoxygenation and hypoventilation) were reproduced.

TD-NIRS homogeneous models, appear to be highly accurate in retrieving cerebral oxygen saturation, but large errors were observed considering haemoglobin concentration. These results suggest that models that account for the heterogeneous structure of probed tissue could increase the accuracy in retrieving cerebral haemoglobin concentration, at the expense of complexity and computational time. Aware of the obtained results, we exploited the BabyLux device, a hybrid TD-NIRS and DCS instrument, to evaluate haemodynamic and metabolic changes of preterm neonates that underwent RBC transfusion, and we investigated the advantages of this hybrid device compared to continuous wave (CW) NIRS instrument, widely used technique in ICU to non-invasively assess cerebral haemodynamic in preterm neonates. A wider range of oxygen saturation levels were measured using CW-NIRS compared to TD-NIRS, suggesting the higher accuracy of TD-NIRS in estimating neonatal cerebral oxygen saturation. Moreover, the use of a hybrid device allowed us to assess the cerebral haemoglobin concentration and cerebral metabolism that were never investigated before, and that could be

key parameters in the comprehension of the effects of RBC transfusions on cerebral health of preterm neonates. Indeed, after the transfusions, a significant increase in oxygen saturation level and haemoglobin concentration were observed, but metabolic parameter seemed to be unaffected by the RBC transfusion, suggesting that eventually the level of anaemia was not so acute to modify the cerebral metabolism in neonates.

Moving to the adult population, due to the different structures of the tissues investigated, a larger penetration depth is needed to assess brain or muscles haemodynamics. We developed a new compact hybrid device that allows to perform measurements at larger inter-fiber distances (i.e. higher penetration depth), maintaining a good level of signal-to-noise ratio with 1s integration time. The performances of the new device were assessed with measurements on phantoms and in-vivo. The obtained results highlight a high level of temporal stability, with a CV for the Db lower than 5% over 3h of measurements; a good reproducibility, with a CV lower than 3% for the Db over two weeks of measurements; and large accuracy in retrieving Db variations: as a matter of fact changing phantom viscosity the Einstein relation was reproduced with R2 of 0.99. However, characterization measurements also highlight the necessity to use correct optical properties (in particular correct reduced scattering coefficient) in the DCS analysis to retrieve the proper diffusion coefficient, a sufficiently high count rate to avoid the low signal level affecting the retrieved dynamic

properties (larger than 40 kcps), and a proper optical probe design to avoid cross-talk between TD-NIRS and DCS module (when 3.5 mW are emitted by TD-NIRS source its distance from the DCS detection should be higher than 1.5 cm). By exploiting this hybrid device, vascular occlusion tests (VOT) were performed on healthy subjects and hypotension and hypertension protocols were executed on neonatal piglets. In both cases the haemodynamic parameters show variations in accordance with literature, demonstrating the ability of the device in monitoring haemodynamic changes in biological tissues.

Finally, the new device was exploited to test the clinical protocol of the VASCOVID European project. Arterial occlusions were performed on 19 healthy subjects, placing the cuff in different positions of the arm, and haemodynamic changes in the thenar eminence were measured. The use of a hybrid device, compared to a CW-NIRS instrument, allowed us to notice unexpected BFI and haemoglobin concentration responses to VOT, suggesting that different probe positions could provide a better biomarker for the progression of COVID-19 disease.

The results presented in this thesis highlight the strong impact that blood flow, haemoglobin concentration and metabolic parameters can have on the interpretation of tissue health, and the advantages of a hybrid DO device compared to commercially available continuous wave NIRS instruments which only enable to assess the oxygenation level.



## LIGHT TRANSDUCERS FOR TRIGGERING AND PROBING THE CELLULAR MEMBRANE

Gaia Bondelli – Supervisor: Guglielmo Lanzani

The manifestation of electrical phenomena in living systems is a fundamental process underlying many biological functions. In these bioelectricity events, cellular membranes play a key role, determining the arising of electrochemical gradients between the cell intra- and extra-cellular media, giving rise to potential differences across the membrane. The understanding of bioelectricity's origin and the possibility of manipulating the activity of living cells has thus attracted considerable scientific efforts, with immense implications in biophysics and neuroscience. In these regards, optical techniques have attracted great interest, due to their high temporal and spatial resolution and non-invasiveness. As most of eukaryotic cells are not

sensitive to optical stimuli, the use of some kind of transduction mechanism is necessary to modulate bioelectricity with light. A convenient approach consists in the use of photoactive materials placed in close proximity of the biological sample and working as transducers, converting the light excitation into electrical, mechanical, chemical, or thermal stimuli. Different kind and shapes of such phototransducers exist, including thin film planar interfaces, micro- and nano-structured particles and molecular photoswitches. During my PhD I've focused on the use of light transducers both for triggering and probing the cellular membrane, in order to study the mechanisms which lay behind cellular

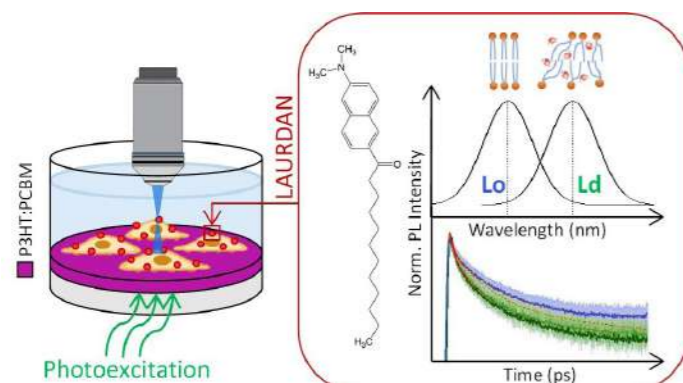
photostimulation. For what regards the membrane triggering, the choice fell on membrane-targeted amphiphilic azobenzene derivatives. Such chemical compounds can undergo light-driven reversible transitions between two conformers, identifying two different states used to trigger cellular processes. Six different azobenzene derivatives were investigated, having a different number of substituents attached to the central azobenzene core or different alkyl chain termination, with the final aim to understand which characteristics were the most suitable to exploit these molecules to provoke an opto-mechanical effect in the lipid membrane.

The molecule named ZIAPIN2, characterized by an azepane ring on one side and two alkyl chains on the other side, emerged as the most performing one. This molecule partitions stably into the plasma membrane where it can work as an efficient opto-mechanical actuator. In particular, while the dark-adapted trans isomer causes a thinning of the lipid bilayer via a dimerization mechanism, illumination with visible light leads to a membrane relaxation that follows disruption of the azobenzene dimers. This, in turn, enables the cell membrane capacitance to be modulated and permits to evoke light-induced neuronal firing in vitro and in vivo. Quasi-Elastic Neutron Scattering measurements were done to study the effects on the dynamics occurring in the picosecond time range and at the molecular level following perturbation in the lipid membrane caused by ZIAPIN2. Coupling experiments carried out both on model membranes and intact cells, we found out that ZIAPIN2 partitioning

produces a general softening of the bilayer owing to its interaction with the lipids, which indicates that the efficacy of ZIAPIN2 in triggering cellular signaling stems from its ability to mechanically perturb the bilayer as a whole, by forming light-sensitive membrane spanning dimers. Afterwards, ZIAPIN2 effect on prokaryotic cell membranes was investigated, in order to validate its use in controlling bacteria proliferation activity. ZIAPIN2 was found to possess a bactericidal action with a Minimum Inhibitory Concentration at which eukaryotic cells do not suffer. Thanks to ZIAPIN2 localization and isomerization in bacteria membrane, the molecule effect can be switched on/off simply through light. These results suggest that non-genetic opto-mechanical triggering of bacteria lipid membrane may lead to a technology for controlling bacterial cellular behaviors using light, providing an antibacterial compound that exhibits some novel and interesting aspects, being ZIAPIN2 not based on existing antibiotics and not relying on existing antibiotics mechanisms. Characterizing ZIAPIN2, beside its triggering properties, we observed that its photophysics is extremely sensitive to the local microenvironment viscosity and polarity. By employing steady-state and time-resolved optical spectroscopies, we found that the azobenzene relaxation pathways are sensitive to the molecular environment and to the lipid membrane composition, which allowed us to exploit ZIAPIN2 photoisomerization as a tool to probe the cell membrane nanoviscosity. Next, I investigated the mechanisms underlying photothermal perturbation of the cell membrane. The plasma

membrane, indeed, can assume different phases, from the solid-ordered phase, to the liquid-disordered and liquid-ordered ones. Changes in phase have a role in cell stimulation, and more in general, membrane perturbation initiates many biological processes. The photothermal perturbation of the membrane achieved using transducers that convert light into thermal energy, eventually heats the cell membrane. In turn, this leads to the modulation of the membrane electrical capacitance that is assigned to a geometrical modification of the membrane structure. However, the nature of such a change is not understood. To find answers to this open question, I employed an all-optical spectroscopic approach, based on the use of fluorescent probes, to monitor the membrane polarity and order directly in living cells under thermal excitation transduced by a photoexcited polymer film, providing solid evidence for the temperature-induced structural modification occurring in the membrane. Additionally, the results suggested that water permeates more favorably the disordered membrane phase, and thus the resulting change in the dielectric response of the plasma membrane might be the ruling phenomenon explaining the temperature-induced enhancement in capacitance. Furthermore, we found evidence that optostimulation mediated by a photovoltaic organic film brings about an additional phenomenon reinforcing the perturbation effect that can be assigned to the surface charging at the biointerface. Such results suggested that optostimulation mediated by organic semiconductors is not simply due to thermal effects, but it is also related to the capability of the

photogenerated charges to polarize the plasma membrane. In conclusion, during my PhD I described how the plasma membrane electrical properties are changed by the use of photoexcited intra membrane molecular switches or by photothermal phenomena. This brought new knowledge in the field of non-genetic cell photostimulation and in innovative neuro-technologies for the study of the central nervous system.



**Fig. 1** Investigation of the mechanisms underlying photothermal perturbation of the cellular membrane. HEK-293 living cells were grown on P3HT:PCBM photoactive films and stained with the polarity-sensitive probe Laurdan. Laurdan chemical structure and schematic representation of the corresponding emission maxima in ordered and disordered phases of the cell membrane are shown. Time-Resolved Photoluminescence measurements, before and during photoexcitation of the polymeric film, allowed us to shed light on thermally induced optocapacitance at the organic biointerface.

## ACTIVE OPTOMAGNETIC BIOSENSING SYSTEM ON CHIP

Piero Borga – Supervisor: Andrea Melloni

Recently, we got hit by a world-wide pandemic that caused deaths, prolonged uncertainty and started a global economic destabilization while in the next years, thanks to the rapidly changing world, we are expecting to see other widely spread threats to happen. Plus, we cannot forget more common health issues and conditions that cause large number in fatalities every year and can be of very different causes: influenza, diabetes, various forms of cancer, immunodeficiency diseases and many more. Early detection of any of these is of fundamental importance to periodically check the patient condition, find a suitable therapy on time or avoid the situation to worsen, so diagnostics in going to be a very important topic in which to focus high quality research. Integrated photonics solutions are rapidly evolving as biosensing and diagnostic platforms from experimental prototypes to market-ready tools. Interferometry-based devices in Silicon Photonics (SiPh) like resonating cavities are showing great potential thanks to the easy integration in CMOS platforms for mass production. Optical platforms exploit the refractive index shift  $\Delta n$  caused by the molecules binding together in proximity of the waveguiding structure. The  $\Delta n$  cause the resonance condition of the cavity to change, producing a shift in the resonating wavelength  $\Delta\lambda$ . Since the molecular binding speed depends on the molecule affinity, the hybridization process takes from few minutes to several hours to complete. This shift has been usually measured scanning the transfer function of the optical structures, one MRR used as sensor and one as reference, extracting the resonating wavelength and calculating

its shift over time. This method, although easy to realize and reliable, is subjected to lot of noise coming from the environment such as mechanical oscillations, temperature variations and refractive index inhomogeneities in the sample. Over the long scanning period, the noise reduces the quality of the information, strongly limiting the Limit of Detection (LoD). Along the label-free detection, in which just the target molecule is detected, a passive label such silica, polystyrene or metal nanoparticles can be used as second binding step to enhance the sensor's response performing a passive labelled measurement. In our laboratory we tested these approaches on a SiPh chip and for our DNA model we obtained a LoD of 1nM concentration, with 2.5 hours long measurements. In collaboration with regional project partners, we realized a diagnostic device prototype to be used at hospital laboratories. The prototype is based on the transfer function scan method with both label-free and passive labelling

approaches, it is semiautomatic, easy to use and has been tested with human plasma from Dengue virus positive patients.

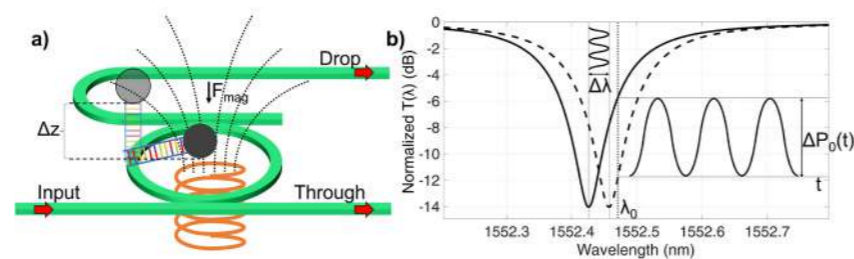
To overcome the issue of long-lasting measurements we developed the OptoMagnetic technique, that performs an active labelling approach to extract the information hours or days after the molecular binding took place, that requires no thermal stability, improves the LoD with respect of the classical method and requires from few minutes down to few seconds for the interrogation process.

The OptoMagnetic technique exploits magnetic nanoparticles (MNP) as labels: an external magnetic field produces an attractive force that moves the labels towards the MRR (Fig. 1a). The modified refractive index over the cavity causes a shift in the resonance. With an AC magnetic field, the physical oscillations are transformed into an amplitude modulation in the optical outputs of the MRR (Fig. 1b). This amplitude, collected by a photodiode across all the

transfer function can be extracted by demodulating it with a lock-in amplifier. Then, the demodulated signal and the slope of the transfer function are used to evaluate the actual resonance shift produced by the oscillating MNP. The measurement can be repeated for both sensing and reference MRR and for different analyte concentrations to obtain a calibration curve that gives a relation between the extracted signal and the quantity of the molecule we want to detect in the sample. The scanning process takes just a couple of minutes and the LoD drops by at least an order of magnitude, from the previous 1nM to below 100pM for our DNA model.

To improve performances even more at lower concentrations, a second technique was developed. In this case, first the transfer function and its slope are evaluated and then the AC magnetic field is briefly turned on. Reducing the filter bandwidth of the lock-in amplifier it is possible to obtain a much cleaner signal that pushes the LoD by at least another order of magnitude, below 10pM concentration. The resulting On-Off signal is very promising to further investigations since it improved, for the SiPh chip we used, the LoD by several orders of magnitude and with a measurement time of just 10 seconds. As last step, we wanted to reduce the complexity of the system towards an easier future prototyping. So first we studied the various options to integrate coils in the SiPh chip to generate the magnetic field closer to the sensing area, with a higher magnetic force, an easier system management and a lower power consumption. With multiphysics simulations we studied the effect of such structures on MNP dynamics and

subsequently on MRR resonances. We then designed and realized the chips with different promising structures to be tested along the electronics meant to control the system. This will allow in future works to implement the OptoMagnetic technique on an optimized platform in an easier way to perform biosensing and diagnostics at the state-of-the-art capabilities in integrated optics.



**Fig. 1**  
**Optomagnetic biosensing concept. a) The biomolecules-MNP system bind above the sensing MRR, an external magnetic field attracts the MNP towards the surface producing a resonance shift. b) An AC magnetic field generates a transfer function oscillation and at the MRR output an amplitude modulation that can be extracted with a lock-in amplifier.**

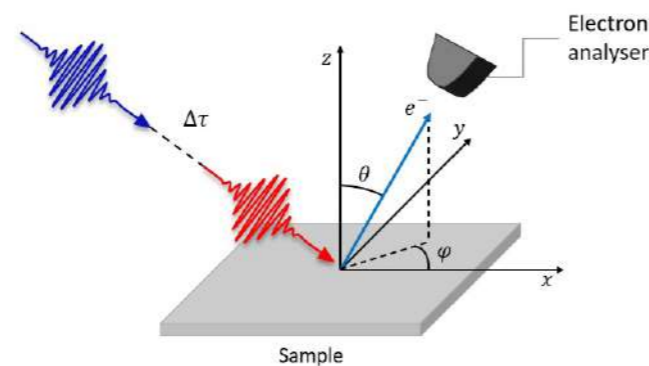
## INVESTIGATIONS OF PHOTO-EXCITED 2D MATERIALS BY COMBINED ULTRAFAST SPECTROSCOPY TECHNIQUES

Arianna Ceraso – Supervisor: Ettore Carpene

The research activity carried out during my PhD course has focused on the exploration and the understanding of phase transitions, and extreme non-equilibrium conditions in two-dimensional (2D) materials such as transition metal dichalcogenides (TMDs) and black phosphorus (BP). In this context, ultrafast spectroscopy is a useful and promising tool to study the origin of complex orders. The main technique that I employed during my PhD is time- and angle-resolved photoemission spectroscopy (TR-ARPES) which, thanks to its energy and momentum sensitivity, allows revealing dynamics of the electronic band structure of the material. A typical TR-ARPES experiment is schematically depicted in Fig. 1. By changing the time delay between the two ultrashort pulses, one can study time-dependent processes taking place after the pump-induced non-equilibrium electronic state with sub-picosecond resolution. Therefore, TR-ARPES enables mapping the transient changes of the electronic structure as a function of electron kinetic energy, electron momentum and time-delay between pump and probe pulses, extending standard ARPES. Besides the femtosecond TR-ARPES, time-resolved reflectivity (TRR) measurements on the aforementioned materials are also performed. Indeed, despite the lack of momentum resolution of the technique, TRR allows a significant understanding about the out-of-equilibrium behavior of the electronic and lattice degrees of freedom, allowing a more extensive knowledge of the material properties. Even though

it exploits the same experimental scheme involved in TR-ARPES, i.e. the so-called pump-probe scheme, the dynamics is retrieved in different ways: photoemission spectroscopy is based on the detection of electrons extracted by the sample, while time-resolved optical spectroscopy detects reflected or transmitted photons. In the last few years, layered two-dimensional materials, such as

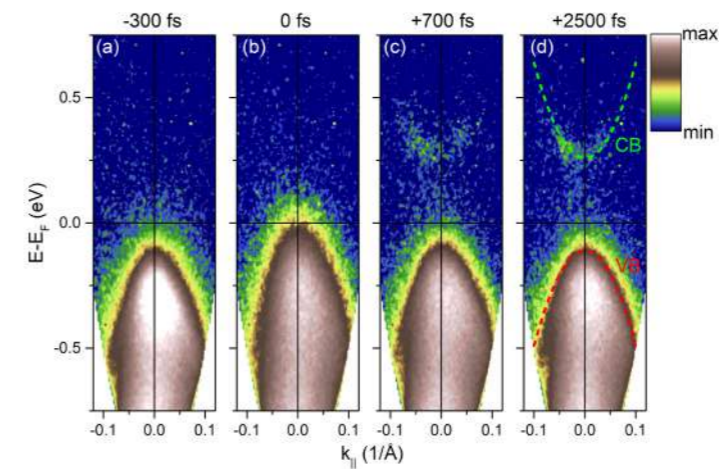
graphene and hexagonal boron nitride (h-BN), have received significant attention due to their potential applications in several fields. Graphene, a single layer of graphite, was the first 2D material to be obtained via mechanical exfoliation from bulk graphite in 2004. Because of its attractive properties, the discovery of graphene has stimulated the investigation of other layered



**Fig. 1**  
**Scheme of a photoemission experiment. Light with photon energy  $xx$  illuminates the sample. As a result of the photoelectric effect, electrons emitted into the vacuum, are collected by an electron analyzer.**

2D materials, which are able to complement the demands related to graphene and can be employed as platforms for exploring new physical and chemical phenomena. Recently, the scientific community has drawn great attention on TMDs, owing to their special electrical, mechanical, and optical properties as well as to their possible technological applications. TMDs are materials of the form  $MX_2$  where M refers to a transition metal and

X indicates a chalcogen element such as sulfur (S), selenium (Se), or tellurium (Te). They form a group of layered compounds where the transition metals are sandwiched between two chalcogen layers. The resulting X-M-X slabs display strong intralayer covalent bonding and a weak mutual van der Waals coupling, which are responsible for a quasi-two-dimensional (2D) behavior. Because of the relatively large number of the feasible transition



**Fig. 2**  
**Room-temperature maps on bulk BP measured by TR-RPES at different pump-probe delays.**

metal and chalcogen combinations, TMDs with various electronic structures can be realized. Among TMDs, the tantalum-based compounds  $TaX_2$  with  $X = S$  or  $Se$  are of particular interest because they are host to coexisting strongly correlated phases including charge density waves (CDWs) and an unusual metal-insulator transition (MIT). These materials exhibit several CDW phases as incommensurate (ICCDW), nearly-commensurate (NCCDW) and commensurate (CCDW), with transition temperatures over a broad range extending from 75 K up to 473 K. The TMD of our interest was 1T-TaSe<sub>2</sub>. In this sample, the NCCDW phase is not observed and there is just a direct transition from the CCDW to an ICCDW phase at 473 K which is accompanied by an in-plane periodic lattice distortion of dimensions and a rotation of 13° with respect to the original unit cell. At lower temperature, below about 260 K, a surface Mott

metal-insulator transition has been observed. TR-ARPES and TRR allowed us to study the interplay between charge density wave (CDW) and Mott phases in 1T-TaSe<sub>2</sub>, revealing that the Mott phase is preferentially linked to the main phonon mode addressed as the CDW amplitude mode. Furthermore, recent temperature-dependent TR-ARPES measurements on 1T-TaSe<sub>2</sub>, within the commensurate CDW phase, give evidence of a phonon splitting of the CDW amplitude mode at low temperature which was interpreted as an experimental hint of a dimerization process in 1T-TaSe<sub>2</sub>. As regarding BP, we investigated this material by TR-ARPES both in its pristine condition and after Cs deposition, revealing a rich photo-induced band dynamics. This material exhibits intricate interactions associated with charge, spin, lattice and orbital degrees of freedom whose deeper comprehension is fundamental for optoelectronic,

electronic and technological applications. BP crystallizes in the orthorhombic structure, where  $sp^3$  orbital hybridization leads to buckled layers normal to the z-axis. This semiconductor has a tunable band gap as a function of surface doping by alkali atoms and strain and exhibits anisotropic electronic and optical properties whose origins are rooted in the puckering of its lattice structure. Fig. 2 shows the dynamics of the electronic band structure of bulk BP recorded at the room temperature along the x-axis. In the first panel, the band structure at negative delay, namely before pump arrival is reported and the valence band, which is completely below the Fermi level, can be seen. At zero delay, a pump-induced shift of the valence band can be observed. Finally, at positive delay, the CB also appears, indicating that the CB states are indirectly populated: indeed, electrons are first excited from the VB to higher levels of the CB by the pump pulse and then they decay towards the bottom of the CB via electron-electron and electron-phonon scattering processes. We found that photo-injected carriers trigger a bandgap renormalization and a concomitant valence band flattening due to Pauli blocking. In the Cs-doped sample, photoexcitation causes a long-lived surface photovoltage that compensates the Cs-induced surface band bending. Thanks to this investigation, it was possible to disentangle bulk from surface electronic states, to establish the surface localization of the conduction band and to clarify the occurrence of band inversion in bulk samples.



## TIME-DOMAIN DIFFUSE CORRELATION SPECTROSCOPY: FROM PHYSICS TO BIOMEDICAL APPLICATIONS

Lorenzo Colombo – Supervisor: Antonio Pifferi

Diffuse correlation spectroscopy (DCS) is an optical technique which, by measuring the speckle intensity fluctuations of coherent light diffused by a turbid sample, extracts information regarding the scatterers' dynamics. Its main biomedical application is the in vivo non-invasive measurement of fluctuation of red blood cells, and thus micro-vascular blood flow (BF).

Since DCS typically uses a continuous-wave (CW) light source, it generally lacks depth sensitivity. Also, a knowledge of the sample optical properties (scattering and absorption coefficients) is required for a correct BF estimation. Time-domain (TD) DCS tackles these problems by using a pulsed yet coherent light source. This might enable a depth resolved BF measurement, by measuring the speckle fluctuations at different time-of-flights. In this work, I contributed to lay the foundations of this technique (TD-DCS), both on the theoretical and experimental sides. In the following, I will briefly summarize the achievements of this thesis work.

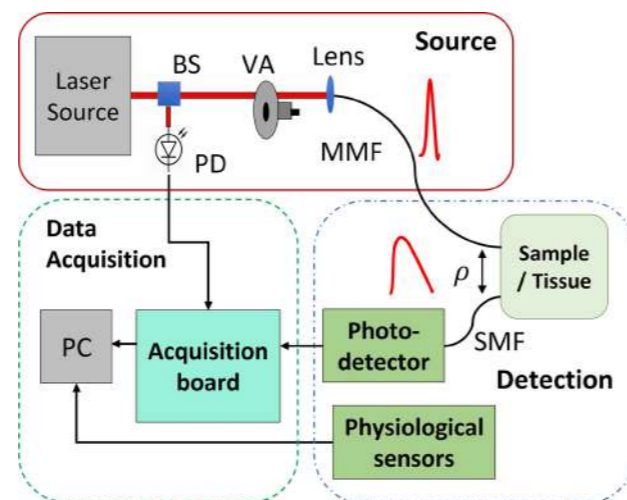
1) Development and validation of a novel theoretical model, which describes the effects of the instrument response function (IRF) and gate width. The model helped in providing physical insights regarding the impact of finite path length (i.e., temporal) resolution on the data, and to estimate in a more quantitative way the blood flow index (BFI).

2) Development and characterization of a versatile lab system, through

an evaluation and comparison of its main components (laser source, photodetectors, acquisition modules). In particular, I showed the impact of the individual components on the quality of the measurements. This was achieved by defining and characterizing suitable figures of merit, in particular the coherence parameter and the BFI. Finally, I suitably integrated additional physiological sensors in the experimental system, see Figure 1. 3) Observation and interpretation of the temporal speckle effect. First, I presented the experimental evidence of this interesting phenomena, namely the "temporal speckle" effect, see Figure 2. Then I provided a simple theoretical interpretation, by adapting analysis approaches which were developed in other fields. Finally, I proposed

a possible biomedical application, by carrying out a cuff occlusion experiment on an adult volunteer. 4) Demonstration of in vivo experiments on human subjects. The first application I considered was a cuff occlusion experiment, which confirmed the suitability of the system to biomedical application. Then, I moved to experiments on the brain, focusing on two protocols: resting state and breath hold. This enabled to observe interesting physiological phenomena, such as the vascular pulsatility, see Figure 3. These in vivo experiments are one of the first reported in the TD-DCS literature.

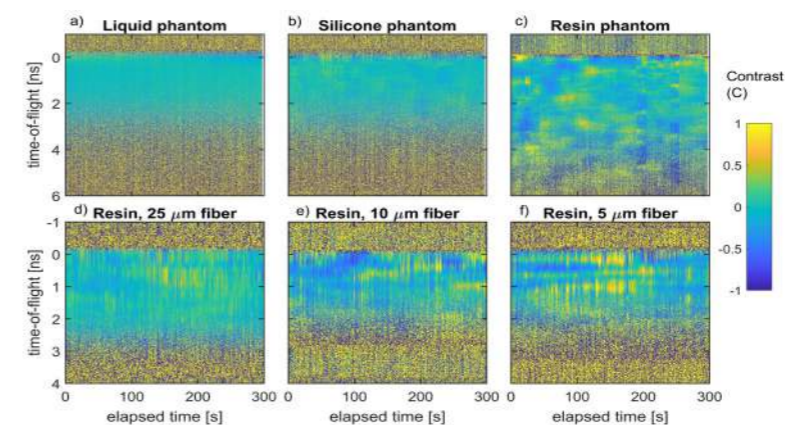
5) In vivo experiments beyond the water absorption peak. Finally, I showed the feasibility of performing experiments in a novel spectral window,



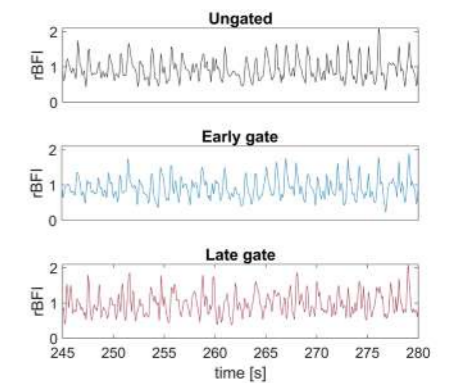
**Fig. 1**  
Scheme of the developed TD-DCS system, characterized by three modular units: Source, Detection, and Data Acquisition.

in particular beyond . The experiments were performed both on tissue-mimicking phantoms and in vivo, on adult volunteers. For performing these experiments, I suitably modified the system (in particular the laser source) for operation in this spectral region. To summarize, with this thesis work I contributed to the foundations of TD-DCS, starting from the physics of the technique, and moving to the experimental and biomedical applications. This work might provide crucial insights for the interpretation of the experimental data, but also help in the design and/or optimization of next generation, high-performance systems. Regarding future developments, there are several interesting directions. First, the development of multi-channel systems. This might enable to increase dramatically the signal-to-noise

ratio, and thus the accuracy and depth sensitivity of the technique. In addition, this might enable to obtain tomographic information of the tissue under study, with a strong impact on several biomedical applications. Second, the development of multi-wavelength systems, which might enable to extract in parallel both the BFI and the concentration of the main tissue constituents (as in diffuse optical spectroscopy/tomography). Last but not least, the development of real-time analysis software, which is crucial in several environments where the measurement is not easily repeatable.



**Fig. 2**  
Observation of the temporal speckle effect for (a-c) different types of samples and (d-f) different detection fiber diameters.



**Fig. 3**  
Observation of vascular pulsatility on the forehead of an adult volunteer, for three different acquisition strategies (Ungated, Early gate, and Late gate).



## DEVELOPMENT OF ULTRAFAST X-RAY SPECTROSCOPY FOR THE INVESTIGATION OF ELECTRON DYNAMICS IN SEMICONDUCTORS

Gabriele Crippa – Supervisor: Caterina Vozzi

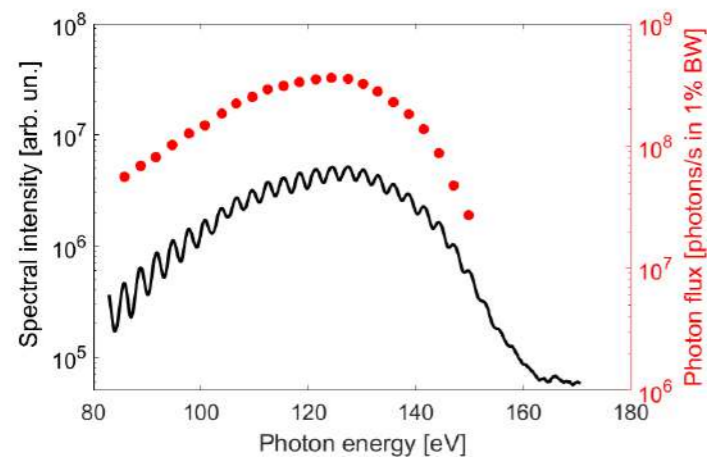
High Harmonic Generation (HHG), arising from the interaction of intense femtosecond laser pulses with noble gases, led to the realization of table-top sources of coherent Extreme UltraViolet (EUV) and Soft-X Ray (SXR) radiation. These sources combine the temporal resolution of ultrafast spectroscopy, generally performed in the visible or IR frequency range, with chemical sensitivity of X-Ray experiments, usually performed at longer time scales. As a result, ultrafast spectroscopy can nowadays be performed with extreme temporal resolutions, down to the attosecond regime (1 attosecond =  $10^{-18}$  sec), and site and chemical selectivity. These peculiar features grant access to purely electronic dynamics in molecules and solids initiated by ultrafast laser pulses and to fundamental processes of light-matter interaction.

One of the most promising all-optical techniques to perform these experiments is nowadays transient absorption in the EUV. In this, an ultrashort laser pulse is used to initiate a target process in the system, exciting it out of equilibrium. The induced dynamics is then probed by a time-delayed ultrashort EUV pulse through its time-dependent differential absorption. However, the full exploitation of ultrafast spectroscopy in the EUV and SXR spectral range is hindered, even today, by the technological complexity of the required setups and the low generation efficiency of the HHG sources, particularly when moving towards higher photon energies. In this PhD work, a new beamline for EUV transient absorption spectroscopy experiments in solids was developed, while overcoming some of these

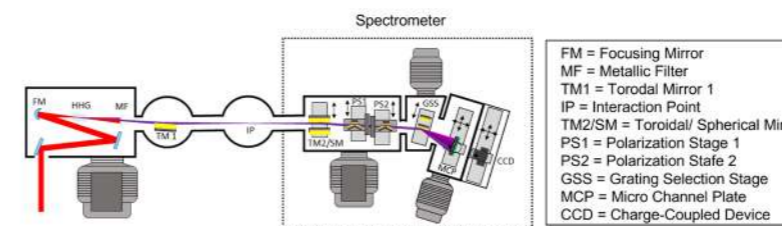
limitations. To increase the HHG efficiency, beyond state-of-the-art, harmonics generation was performed in novel microfluidic devices, developed in collaboration with the group of Dr. R. Osellame and Dr. R. M. Vazques from CNR-IFN in Milan. This platform grants not only a dramatic increase of the HHG efficiency, but also a fine control over the gas density in the harmonics generation region. Therefore, quasi-phase-matching strategies based on gas density modulation can be implemented for shaping the EUV spectrum. These have been implemented with the theoretical and numerical support of Prof. A. Frezzotti from DAER in Politecnico di Milano, for the gas fluid dynamics, and of Dr. V. Tosa from INCDTIM in Cluj-Napoca, for the field propagation inside the microstructure and the HHG model. In the future, microfluidic devices could lead to the engineering of the generation process and the integration of different functionalities related to ultrafast spectroscopy experiments. This will ultimately pave the way to the realization of Lab-On-a-Chip (LOC) approaches in attosecond science. In a transient absorption experiment, the pump and probe beams are focused on an interaction point and the transmitted EUV radiation is analysed by a suitable spectrometer. In the new beamline, the harmonic generation process was driven by VIS-NIR pulses (150  $\mu$ J, 10 fs) obtained through self-phase modulation in an Ar-filled hollow-core fiber and subsequent dispersion compensation using chirped mirrors. A portion of this beam is used as a pump for pump-

probe experiments and its energy can then be tuned with the combination of a halfwave plate and an uncoated window at Brewster angle. Concerning the HHG section, the spectral range accessible to standard spectrometers is frequently limited to either low or high-energy photons, which is not suitable for many spectroscopic applications (e.g., to simultaneously access valence and core energy levels). Moreover, these systems generally work in stigmatic configuration to focus the harmonic signal on the detector, thus increasing the signal-to-noise ratio. On the other hand, this precludes the measurement of the EUV divergence, which can be important for some experiments. Lastly, the characterization of the harmonics polarization state is frequently not available, hindering the investigation of ultrafast electron dynamics in chiral systems, such as biologically relevant molecules and magnetic materials. In this PhD work, a new design of a flexible EUV spectrometer was developed. This can be remotely tuned, without any need to realign optical elements

or to break the vacuum. The selection between two gratings enables detection of the whole 1-100 nm spectral range, while the selection between a toroidal and a spherical mirror allows the spectrometer to work either in stigmatic or astigmatic configuration. Moreover, a two-stage EUV polarimeter can be independently inserted for the full characterization of the harmonics in terms of its Stokes parameters down to 12 nm. The detector was also upgraded from a single stage to a double stack Micro Channel Plate (MCP) for increased gain and dynamic range. Both the MCP and the CCD can be remotely moved to accommodate the whole dispersion curve of the two gratings. This flexible and user-friendly spectrometer will facilitate the realization of novel experimental schemes. This beamline will be employed for the study of electron dynamics in molecules and condensed matter. Firstly, simple semiconductors will be addressed as an experimental benchmark. Then, EUV transient absorption will be performed to unveil electron dynamics in advanced and innovative materials.



**Fig. 1**  
EUV spectrum generated in the microfluidic device, with absolute photon flux calibration. The generation was performed in He gas at a backing pressure of 1 bar.



**Fig. 2**  
Design of the beamline, with the flexible HHG spectrometer, developed during this PhD work.

## CONJUGATED POLYMER NANOPARTICLES AND DEVICES FOR OPTICAL CONTROL OF CELL METABOLISM AND FATE

Federico Gobbo – Supervisor: Maria Rosa Antognazza

The capability to control and modulate the activity of biological systems is considered a major target in biomedical technology research, because it might lead to a deeper understanding of specific functions and to innovative strategies to manage dysfunctions. Optical modulation provides, respect to traditional electrical methods, unprecedented spatial and temporal resolution, lower invasiveness of treatment and higher selectivity. Since living cells are transparent to light, it is necessary to make recourse either to optogenetics or to light-sensitive smart materials. Optogenetics tools require viral gene transfer, raising important safety issues for application in human patients. Light-sensitive materials, instead, hold the potential to circumvent this major issue. Organic semiconducting polymers are arising as optimal candidates as exogenous optical transducers, due to their distinctive chemical-physical properties, geometrical adaptability, biocompatibility and their peculiar optoelectronic properties of semiconductors. In addition, they can be easily functionalized to enable specific probing and sensing capabilities. They absorb light in the visible and near infrared (NIR) spectral windows and support charge photo-generation. Phototransduction mechanisms can be mediated by thermal charges, electrochemical reactions and capacitive charging. Recent works have demonstrated their reliability in the modulation of cells, tissues and even animal behaviour.

The aim of this thesis is to develop light-sensitive devices based on organic

semiconductors able to modulate, with high efficiency and selectivity, the biological activities of living cells. To achieve this purpose, a detailed investigation of the interfacial photo-physical phenomena and of the phototransduction mechanisms is needed.

In the first part of the thesis, results obtained with polymer beads are reported. Polymer NPs can be internalized inside cells and provide a remarkable spatial resolution. They can be prepared in water based solution and in sterile condition, suitable for biological applications. They show high brightness and they have been mainly employed for in vivo and in vitro imaging or for drug delivery applications. Only very recently they started to be used as photo-transducers. Low band-gap semiconducting polymer NPs, based on poly-cyclopenta-dithiophene-benzothiadiazole (PCPDTBT), were prepared through the miniemulsion method. The absorption and emission spectra are located in the red region of the visible spectrum and in NIR; at these wavelengths the auto fluorescence of biological matter is lower and the tissue penetration is higher, therefore these NPs are strongly appealing for potential in vivo applications. NPs were synthesized starting from an amphiphilic rod-coil block copolymer composed of PCPDTBT as the rigid block, while the coil segment consists in a short chain of poly-4-vinylpyridine. The latter is hydrophilic and allows to fabricate NPs based on a hydrophobic polymer avoiding the need of surfactant. NPs starting from the pristine PCPDTBT were also synthesized,

adding a surfactant, polyvinyl alcohol, to investigate the effects of the presence of a surfactant. The nano-dimensions of the polymer beads were confirmed by dynamic light scattering measurements and scanning electron microscopy images. Upon illumination with visible light in the correspondence of the absorption peak, NPs dispersed in water generate a photocurrent signal. The HOMO and LUMO energetic levels of PCPDTBT are well aligned with the reduction potential of oxygen towards superoxide radical anion, this reaction being the origin of the photocatalytic current recorded in aqueous conditions. The photocurrent has a larger amplitude in case of surfactant free NPs. Also the photoinduced absorption spectroscopy measurements, performed on NPs dispersed in water, show that, in case of surfactant free NPs, the amplitude of the signal attributed to charged states is higher. Thus, the presence of the surfactant impacts both on the photogeneration of charged excited states and on the charge extraction efficiency. Secondary line cell models have been treated with NPs. Both the NPs with and without the surfactant internalize within the cell cytosol, without affecting proliferation. The functional interaction between cells and polymer beads upon optical excitation has been studied by fluorescence imaging experiments. In case of surfactant free NPs, the photo-electrochemical activity generates intracellular Reactive Oxygen Species (ROS), at non toxic levels. ROS regulate different biological functions as blood pressure modulation and metabolism regulation; alteration

in their concentration might lead to pathological conditions. It has been observed that, in case of NPs based on a different conjugated polymer, poly(3-hexylthiophen) (P3HT), the variation in ROS concentration deterministically triggers modulation of intracellular calcium ion flux, successfully controlled at single cell level. Calcium fluxes also play a fundamental role in cell metabolism and inter-cell communication processes. They influence the activity of secondary messengers, which in turn trigger many cellular functions, as muscular contraction, proliferation, differentiation or gene expression. Therefore, the capability of polymer NPs to produce ROS by on-demand illumination and to modulate calcium dynamics might open the path for studying biological processes with a minimally invasive procedure and with unprecedented spatiotemporal resolution, laying the foundation for developing novel therapeutic approaches.

In order to increase the photocatalytic activity of P3HT NPs, core shell NPs were fabricated through the double miniemulsion method. The core is made of poly (3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT-PSS) and the external shell is made of P3HT. According to the energetic levels, the photogenerated holes are transferred to the PEDOT:PSS core, thus reducing the recombination processes in the P3HT shell and increasing charge separation. As a result, the number of electrons at the interface with the aqueous electrolyte that can reduce the oxygen increases and a larger photocurrent is measured. Polymer NPs have also

been tested in vivo in *Hydra Vulgaris*, an invertebrate animal model that displays a remarkable regeneration efficiency. ROS concentration plays an important role in the regeneration process, and it has been observed that the regeneration is accelerated in case of animals treated with P3HT NPs and photostimulated.

In the second part of the thesis, results obtained with three-dimensional light-responsive architectures are reported. High aspect ratio polymeric pillars, based on P3HT, were fabricated through the push-coating technique. The microstructured bio-interface allows to combine the optical to the mechanical stimulation, and the three-dimensional architecture resembles more closely the in vivo cellular environment. These devices have been tested with primary line cell models as astrocytes and neurons. Cells cultured on top of polymer pillars display a remarkable change in the cell morphology and a sizable enhancement of the membrane capacitance due to the cell membrane thinning in correspondence to the pillars' top surface. Cellular viability is not affected. As in the case of NPs, upon photostimulation it is possible to modulate intracellular calcium ions fluxes. Moreover, combined action of nano/microtopography and visible light excitation leads to an effective modulation of neuronal growth and orientation: neurons cultured on polymer pillars, upon exposure to optical excitation, show a significant increase in both neurite and axon length. Therefore this device might open up the opportunity to optically regulate cell growth, proliferation and

differentiation in a wireless, repeatable, and spatio-temporally controlled manner, opening the way to further implementation and progress in regenerative medicine.

# INTEGRATION OF LEAD-FREE PIEZOELECTRIC KXNA1-XNB03 ON SILICON FOR MICROACTUATOR TECHNOLOGY APPLICATIONS

Chiara Groppi – Supervisor: Marco Asa

Piezoelectric materials command a huge market in fields such as information technology/robotics, testing transducers and measurement, piezoelectric sensors, acoustic devices and resonators, and many others. In this framework,  $Pb(Zr_{x}Ti_{1-x})O_3$  is the most widely employed for ceramics and thin films for many application devices in electronics because of its excellent piezoelectric properties. However, due to the rising of numerous health concerns regarding the toxicity of Pb, regulatory agencies are encouraging the elimination of toxic substances from electronic devices to reduce the impact on environment and health. The lead-free piezoelectric materials competing for the same applications as PZT started to be investigated, such as  $KxNa_{1-x}NbO_3$  (KNN),  $Bi_{0.5}Na_{0.5}TiO_3$  -  $BaTiO_3$  (BNT-BT), and  $BaxCa_{1-x}ZryTi_{1-y}O_3$  (BCZT)-based materials.

The aim of this research has been the growth, characterization and optimization of  $KxNa_{1-x}NbO_3$  (KNN)

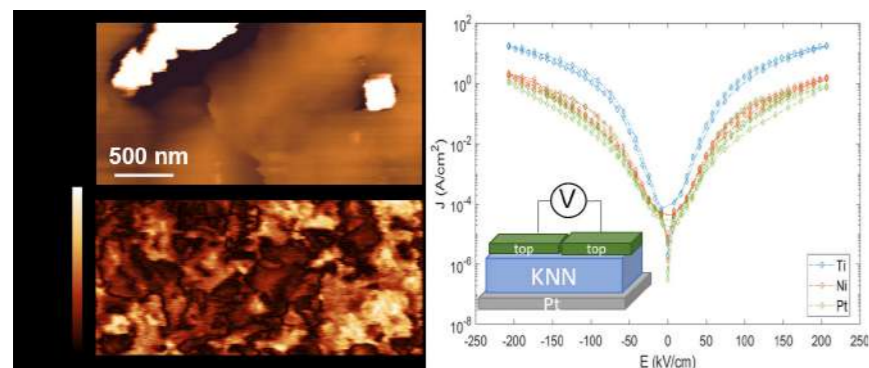
piezoelectric thin films. KNN is a perovskite with a structure of the type  $ABO_3$ , made up of a solid solution of ferroelectric orthorhombic KN and antiferroelectric orthorhombic NN. It displays a high Curie temperature (around  $400^{\circ}C$ ) with respect to other lead-free piezoelectrics, and this makes it an eligible alternative candidate to PZT for the realization of a great variety of MEMS devices with piezoelectric thin films (e.g. actuators and transducers). Besides, similarly to PZT, the phase diagram presents a vertical Morphotropic Phase Boundary between two different ferroelectric orthorhombic phases where piezoelectric and dielectric properties are experimentally found to exhibit exceptional peaks. Such phase boundary is located at a composition of 50% Na and 50% K. For the purpose of the growth optimization, Pulsed Laser Deposition technique was employed with a Nd:YAG laser. Growth parameters were varied and co-varied to study their influence

on the deposited film structure and composition. The employed substrate was the industrial standard  $Pt(111)(100\text{ nm})/TiO_2/SiO_2(700\text{ nm})/Si$ , the same that is commonly used for PZT, and KNN(001) orientation was targeted for best polarization performances. The investigated KNN thin films have an average thickness of 300 nm. Different surface preparation processes of the substrate template were tested to investigate the effect on KNN films, including ex-situ plasma cleaning in Ar and/or  $O_2$  pressure and in-situ annealing in vacuum and  $O_2$  pressure. The study revealed the relevance of the Pt template substrate in determining film morphologic quality and electric, ferroelectric, and piezoelectric properties. As a matter of fact, in-situ vacuum annealing for an optimized time of 20-30 minutes is able to greatly improve thin film planarity and uniformity, investigated with a scanning electron microscope (SEM), and promote (001) growth orientation, as confirmed by XRD measurements. Moreover, leakage current measurements on  $40 \times 40\ \mu m^2$  Ti top electrodes show that the films grown after an in-situ vacuum annealing of the substrate thanks to their compactness and higher degree of texturation display leakage current densities of around one order of magnitude smaller with respect to films grown on untreated substrates i.e. moving from  $10^{-2}$  A/cm<sup>2</sup> to  $10^{-3}$  A/cm<sup>2</sup> with an applied electric field of 50 kV/cm (in the neighborhood of the expected coercive field of the ferroelectric polarization loop). Ferroelectric measurements by switching current

method on the fabricated micro-capacitors show hysteresis loops with remanent polarization of 3  $\mu C/cm^2$ . Local characterization of piezoelectric properties was performed by means of Piezoresponse Force Microscopy (PFM). Maps of spontaneous ferroelectric domains were obtained, confirming (001) orientation, and the measured piezoelectric coefficient  $d_{33}$  is about 80 pm/V, comparable to the highest values reported for state-of-the-art undoped KNN thin films.

Furthermore, the research was focused on phase evolution as well as performance enhancement of such material with chemical modification through dopants. Upon inspecting doping possibilities, Li doping was chosen because, when present in the matrix in a molar quantity of around 0.02, it is able to promote the formation of phase boundaries at room temperature to increase piezoelectric performances. Doping was achieved by co-ablating the KNN target and a slice of  $LiNbO_3$  single crystal. The behavior of Li into the lattice was investigated by means of Secondary Ion Mass Spectroscopy (SIMS), which revealed a phenomenon of severe interdiffusion and accumulation at the surface. This shed light on the mechanism of incorporation of such very mobile species into the lattice. Therefore, Li doping requires high control of the diffusion mechanisms and of the incorporation of the dopants into the lattice, which can have a severe impact on leakage currents. PFM measurements showed a piezoelectric coefficient of 80 pm/V, indicating that  $Li^+$  ions likely accumulate at interstitials,

defects and grain boundaries, and as such do not influence piezoelectric measurements performed on top of a grain. Finally, the role of interfaces was investigated, by employing both different substrates and different top electrode materials. In particular, epitaxial growth on  $Nb:STO(001)$  substrates was found to introduce a high degree of strain that clamps the thin film reducing its piezoelectric performances ( $d_{33} = 40\text{ pm/V}$ ). Moreover, Pt, Ni, Cr and Ti metals for the top electrode material were deposited on the same KNN thin film grown onto  $Pt(111)$  and leakage and ferroelectric measurements were performed and compared. The device was found to behave as a rectifying Schottky diode at high fields ( $E > 20\text{ kV/cm}$ ). The use of Pt and Ni electrode materials was able to reduce thin film leakage currents by up to one order of magnitude with respect to Ti, i.e. from  $10^{-3}$  A/cm<sup>2</sup> to  $10^{-4}$  A/cm<sup>2</sup> for  $E = 50\text{ kV/cm}$ . This indicates the role of interfaces can be decisive for electrical behaviour of the microcapacitors: atomic metal interdiffusion into the dielectric possibly due to high-temperature growth and/or post-growth annealings, the quality of the interface and the conduction parameters intrinsic to the metal (e.g. the barrier height) have a high influence on the amount of mobile charge carriers into the thin films.



**Fig. 1**  
On the left, topography and PFM map of the  $d_{33}$  from KNN/Pt. On the right, comparison of IV curves with different top electrodes.

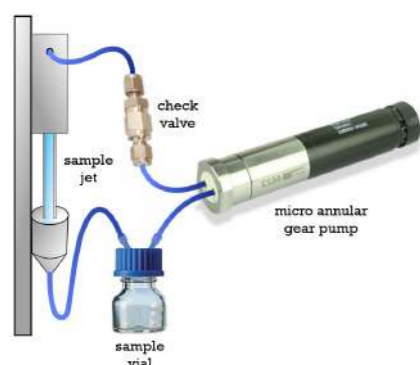


## ULTRAFAST UV SPECTROSCOPY OF BIOMOLECULES

Piotr Kabaciński – Supervisor: Giulio Cerullo

UV light is present in our daily lives as part of the solar radiation reaching the Earth's surface. Every day, the UV photons interact with molecules contained in skin cells, potentially leading to pathogenic lesions. In this work, we focused on DNA and RNA molecules that code and transfer the genetic information of how to build proteins out of amino acid chains. To study their photophysical properties, we have constructed a UV transient absorption (TA) setup, optimized for tunability and sub-30-fs temporal resolution.

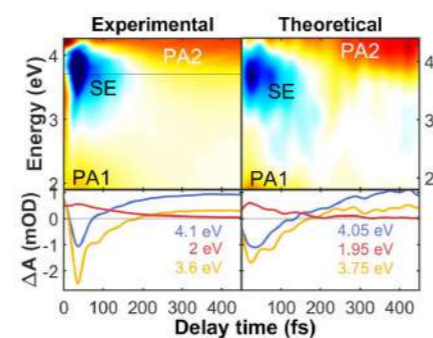
The setup uses pump-probe geometry, where two subsequent pulses hit the sample, one in the tunable 250–300 nm region called the pump, achieved by second harmonic generation of the output of broadband noncollinear optical parametric amplifier, and the other, called the probe, with the total UV-VIS coverage of 260–650 nm that comes after a specified time delay. By exciting the sample at one of its absorption peaks and then tracking its absorption response in a broad spectral



**Fig. 1**  
Wire-guided jet setup.

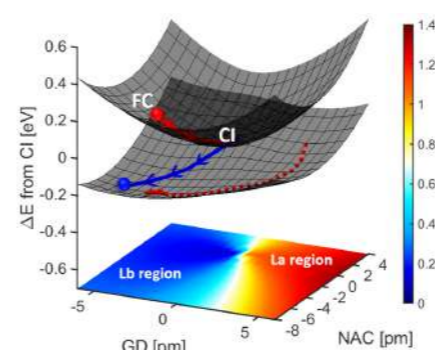
window, we can study how the state of the molecule changes in real time. To maximize the available temporal resolution of the setup, wire-guided jet system has been developed for continuous sample flow in a thin laminar jet configuration, which avoids the interaction of UV pulses with the glass of the usually used cuvette and allows sample thickness down to 100  $\mu\text{m}$  (Fig. 1). The resolution has also been improved through optimizing the concentration of the samples, carefully controlling dispersion, and correcting mechanical inefficiencies of the delay stage. Thanks to these improvements, we can not only track the electronic response, but also simultaneously we observe some of the vibrational modes. We focused our attention on three sets of biomolecules. First, we studied two RNA nucleosides, uridine and 5-methyluridine. As fundamental building blocks, these molecules have been the subject of many studies in the past, but none fully explained their behavior. Our combined experimental and theoretical work (collaboration with University of Bologna) finally solved the remaining questions. We found that the sub-100-fs time constant dominating the spectral dynamics of uridine (Fig. 2) is due to coherent ballistic motion towards conical intersection with the ground state and resolved the debate for 5-methyluridine, showing that the slow  $\sim 1$  ps component is responsible for the transfer to the ground state, while the population of the dark  $n\pi^*$  state is negligible. The difference in decay times of these two molecules can be associated with bulky methyl group motion and its interaction with the solvent, that causes a dynamic change in the potential energy landscape. Second project involved a group of

four epigenetic DNA nucleosides that are responsible for modulating gene expression. Here we studied the complex decay pathways of modified cytidine molecules and observed how different substitutions influence the dynamics. We found that while the behavior of 5-methylcytidine and 5-hydroxymethylcytidine is very similar, the other two epigenetic cytidines show a different story. In 5-formylcytidine we see competition of intersystem crossing and internal conversion, leading to efficient population of a long-lived triplet state that could be potentially responsible for DNA damage, and in 5-carboxycytidine we recorded a ballistic decay to the ground state, similar to the one observed for uridine. This work can help with understanding epigenetic DNA photodamage as well as developing potential therapeutics. Finally, we looked at tryptophan, which is one of the amino acids that are used to build proteins based on the DNA code. Being the brightest chromophore among the three natural aromatic amino acids, it can be utilized as a local



**Fig. 2**  
TA maps for uridine showing extremely fast decay of the signals corresponding to the excited state.

probe for protein dynamics. We have pumped tryptophan at two different wavelengths to distinguish the response from its two lowest excited states La and Lb, but found no difference in the resulting TA maps. The theoretical collaboration helped us explain that this is due to an early conical intersection present on the wavepacket's path soon after excitation to the La state (Fig. 3). From this point on, the wavepacket can then dynamically explore the lower potential energy surface, occupying both Lb and La regions. Due to the La state having polar character (while Lb is neutral), it polarizes the solvent around it, which tilts the bottom potential energy surface and flips the state energy ordering, bringing the La region below Lb, thus facilitating transfer back to the La state in 200 fs. Afterwards we observe further relaxation of the La state on the 1 ps scale. Even though it cannot be seen in the absorption changes, the vibrational fingerprint recorded in the measurement confirms it. The characteristic phase jump in oscillations, located at the peak of the emitting band can be tracked,



**Fig. 3**  
Early dynamics after excitation of tryptophan to the La state.

redshifting over time with the same trend as the computed La emission shift. This confirms experimentally that some population is always present in the La state and drives the solvent relaxation. As we show, Tryptophan dynamics are very sensitive to the solvent environment and with TA spectroscopy we can precisely track them even in the sub-picosecond range to act as a local probe of protein dynamics, also on the shortest timescales.

In conclusion, the constructed UV TA setup provided us with many insights about the primary photophysical processes in RNA, DNA and amino acid molecules. This knowledge of the basic components can be extended further by studying DNA strands, G-quadruplexes and proteins.

## TIME-DOMAIN DIFFUSE OPTICAL SPECTROSCOPY TOWARDS INDUSTRIAL DEPLOYMENT.

Michele Lacerenza - Supervisor: Davide Contini

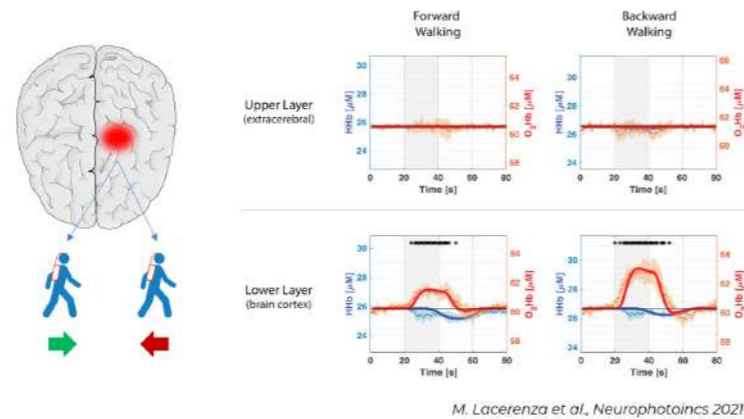
The complexity of our body is outstanding, and since the very beginning, humankind has developed methods and technologies to improve the understanding of our physiology, driven by the desire of defeating diseases and an insatiable curiosity. Enormous advances have been achieved in clinical diagnosis. Novel technologies enable us to have high detail 3D images of most organs of our body and can retrieve a clear picture of our health at a given timeframe. Less is although known about what happens to our body in action. Most non-invasive medical devices, that can access our brain and muscle behavior, are very expensive, bulky, and require the subjects to stay still during the examinations (e.g. fMRI and PET), this prevents us to know how our organs behave in real-life conditions. Our neurons need oxygen to operate, and brain behaviors can be recorded by measuring regional cerebral hemodynamics thanks to the neurovascular coupling mechanism. Our muscles functions are also dependent on oxygen delivery. Accessing tissue oxygenation is therefore paramount to improve our understanding of humans physiology. Time-domain near-infrared spectroscopy (TD NIRS) exploits the temporal shape modification of picosecond laser pulses diffusing in human tissue, to retrieve hemodynamic properties up to 3 cm depth. Compared to more common diffuse optics (DO) techniques, TD-NIRS can disentangle absorption and reduce scattering values, leading to more accurate and precise DO measurements, in addition,

it is less sensitive to motion artifacts. The main limitations of TD-NIRS are its complexity and bulkiness that prevent it to widely spread in the clinical environment.

My efforts have been focused on the development of a novel, compact TD-NIRS oximeter, that could be easy to use and provide direct access to real-time human tissue oxygenation in "outside of the lab" conditions. The device was deployed and tested, showing promising results also in comparison with other state-of-the-art systems. It was employed in in-vivo measurements targeting motor disorders, one of the big plagues of the modern world representing high expenses for the healthcare system of all countries. A deeper knowledge of how neuromotor

mechanisms behave is needed to tackle this issue and our technology can give a contribution to that by monitoring motor cortex activity in freely moving humans.

My studies, performed in collaboration with physiologists and physiotherapists, aimed to record the functional activation of the motor cortex area in exercise widely used in clinics, such as walking, arm motions, sitting, and standing, pilot measurements were performed on healthy subjects. The device showed to be effective and accurate in recording functional brain activation unveiling basic knowledge on brain functions in everyday-life conditions. It is the first time, to our knowledge that the cerebral motor cortex of healthy subjects was measured by TD-NIRS during freely moving walking exercises Figure 1



**Fig. 1** Haemodynamic activation of the motor cortex during backward and forward walking tasks. Results report the average activation over 5 repetitions of the exercise, task period in the gray area. The non-invasive probe was placed on the C1 position (red spot on the brain sketch). Results show the hemodynamic contribution (oxygenated, red and deoxygenated, blue, hemoglobin) at two depths: superficial tissue layers and cerebral cortex (where the activation takes place).

As side projects, the system was used in other DO applications, in the veterinary field, and the food and agriculture sector. We entered veterinary clinics, to assess equine muscles hemodynamic during stressful operations and diagnosis, lowering the risk of muscle damages due to hypoxia or ipo-perfusion of blood Figure 2. Furthermore, thanks to the ability of TD-NIRS to non-destructively record the concentration of chlorophyll in the pulp of fruits, we studied the ripening evolution of pears during post-harvest conservation in controlled atmosphere in the framework of the ESPERA project.

The excellent findings we achieved as well as the interest in technology able to satisfy the unmet need of assessing deep tissue hemodynamics lead us to the foundation of a start-up company, PIONIRS s.r.l. spin-off of Politecnico di Milano. The company aims to develop

and commercialize the next generation of time-resolved tissue oximeters for clinical use making TD-NIRS technology accessible to the world. Thanks to industrial support, it was possible to have access to multiple replicas of time-resolved oximeter products and contribute to developing specific procedures for their quality assessment. Indeed, well-structured protocols are nowadays lacking and will be cardinal in the future of industrial DO devices.



**Fig. 2** Compact TD-NIRS device recording muscle hemodynamic on a sedated horse during a surgical operation. The compact TD-NIRS device is in the front plane (over the small wooden table, with an orange shelf). The optical probe (orange wires) is placed on the left equine triceps.

## DOPED SEMICONDUCTOR NANOCRYSTALS FOR INFRARED SOLAR ENERGY HARVESTING

Fabio Marangi – Supervisor: Francesco Scotognella

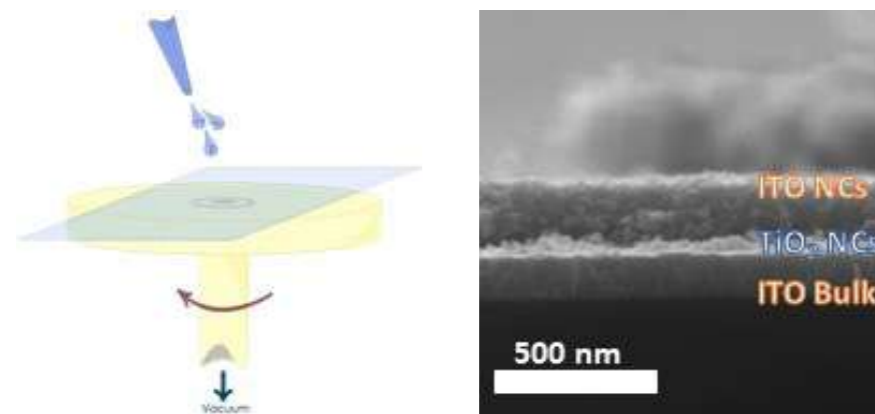
The sun is a huge source of energy. However, only part of it is actively exploited by photovoltaic devices to produce electric power. As a matter of fact, nearly 45% of solar radiation (Near-Infrared), which at the ground level reaches around 1 kW/h, is lost due to spectral losses of silicon-based solar cells or problems regarding conversion efficiency. It is also in order to find a solution to this problem that the scientific community has put a lot of effort in the past two decades in the research revolving around photovoltaics. The greatest amount of effort has been channeled towards the optimization of already existing technologies in order to improve power conversion efficiency, both by investigating alternative device architectures and

by making use of novel materials, also to reduce environmental impact of production processes, the amount of industrial waste and obtain state of the art, efficient devices. Among the many materials showing photovoltaic behavior, those identified as the more promising ones belong to the category of organic semiconductors and lead halide perovskites. Nowadays, solar devices fabricated by making use of these materials show conversion efficiencies comparable with those of well-established, long-lasting technologies based on Silicon. Moreover, fabrication is carried out exploiting wet chemistry processes (Fig. 1- a), which have the advantage of being easy and straightforward and allow the deposition of the materials also on flexible

substrates. However, besides showing some atmospheric stability issues, those devices still focus on harvesting the visible part of the solar spectrum, with very few devices stretching to the nearest infrared, without being optimized for its absorption. Noble metals nanoparticles, such as silver and gold, show collective oscillations of conduction electrons defined localized surface plasmon resonances (LSPRs). Those are associated with near-field enhancement effects in the vicinity of nanoparticles. As a characteristic feature of LSPRs, the resonant wavelength can easily be controlled by changing the size and shape of the NPs. Integrating plasmonic nanoparticles with semiconductor substrates introduces strong optical resonances that extend and enhance the spectrum of photocatalytic and photovoltaic activity. Plasmons excited in the metal create a high concentration of hot electrons which can be injected above or tunnel through the thin Schottky barrier formed with the semiconductor, generating a current. The theoretical power conversion efficiency enhancement achieved can be almost 40 times larger than that of direct illumination while utilizing a broad spectrum of IR to visible wavelengths. Anyhow, those third-generation solar cells need to compete in the visible range, where the market is flooded by many different, already established technologies. That is why ongoing research is focusing on heavily doped semiconductor nanocrystals (NCs) which show broad LSPR absorption bands in the Near-Infrared (NIR). The material which aroused more interest

among non-metallic plasmonic materials is the Indium Tin Oxide (ITO), which has very high carrier densities and shows plasmonic behavior with LSPR absorption in the NIR. ITO has been coupled with wide band-gap semiconductors like Titania and Tin oxide in order to extract LSPR-generated hot-electrons and fabricate transparent photovoltaic devices. The first year of my Phd focused on the optimization of the fabrication process and characterization of the basic physical properties of the materials, including morphology, position of the LSPR peak and so on. Many trials have been performed to obtain compact and homogeneous thin films with complete coverage of the substrate. The recipe for the fabrication has been standardized in order to obtain films having always the same characteristics. The chosen fabrication process also allows stacking of one material on top of the other (Fig. 1- b), making it possible to fabricate interfaces among different materials. Later, experiments focused on obtaining films starting from blends of Nanocrystals that could lead to the fabrication of films resembling polymeric bulk heterojunctions, which are known to be the optimal morphology for charge separation and transport. At the same time, it was possible to deepen our knowledge on ITO optical and electrical properties. Thanks to some collaborators it was possible to perform spectroscopic ellipsometry measurements and modelling to give a detailed description of the response of a thin film of ITO NCs fabricated via spincoating. Those measurements were helpful to retrieve

the complex dielectric function of the material in the form of NCs thin film up to 2500 nm. The effective dielectric constant shows the possibility of tuning the plasma frequency and the epsilon-near-zero condition of the film. The next steps towards a better understanding of the behaviour of the NCs depending on the surrounding dielectric environment include the fabrication and analysis of bi-layers and blends of ITO NCs and other wide-band gap semiconductors. Along with doped semiconductor nanostructures, also other promising NIR responsive materials were taken into consideration during my PhD, including Digenite (Cu<sub>5</sub>S<sub>9</sub>) and Black Phosphorus (BP). The deposition of those nanomaterials in the form of a measurable sample was challenging but ultimately led to some results, which allowed us to their optical characterization.



**Fig. 1**  
**a) Spincoating is the main fabrication technique for lead halide perovskite-based and organic photovoltaics. It allows the deposition of homogeneous thin films.**  
**b) Bi-layer of TiO<sub>2</sub> NCs and ITO NCs on top of a commercial ITO/Glass bulk substrate. Thin films were deposited through spincoating of nanocrystals inks.**



## METAL OXIDE NANOPARTICLES BASED DISTRIBUTED BRAGG REFLECTORS FOR ELECTRO AND BACTERIAL-CHROMISM

Liliana Moscardi – Supervisor: Francesco Scotognella

In recent years, the control of the optical properties of materials has aroused great interest from the scientific community. A huge number of new technologies can be obtained by engineering materials that respond to electromagnetic radiation, so a great effort was put into the theoretical and experimental development of these structures.

Photonic crystals (PhCs) represent a class of materials that allows the control of the propagation of light in a wide range of applications, from optoelectronics to biosensing. They are periodic structures with high symmetry, in which constituent materials with different refractive indices show a repetition along one, two or three dimensions. The periodicity of the dielectric permittivity (or refractive index) in one or more dimensions generates an interference of the incident and scattered electromagnetic waves, leading to the formation of the photonic band gap (PBG), i.e. wavelengths prohibited for photons. This leads to the generation of structural reflection colours, called structural colours, which are not generated by the presence of dyes or pigments but only by the periodicity of the structure; an effect widely present in nature, such as in opals, Morpho butterflies and marble berries. The spectral position of the PBG can be tuned by acting on the refractive index of the constituent materials or on the geometric parameters of the lattice. Therefore, the optical properties are easily modifiable by engineering these parameters, allowing to customize the development of light through the

material.

During my PhD, I focused on the fabrication of one-dimensional photonic crystals, also called Bragg stacks or Distributed Bragg Reflectors (DBRs), and on the possibility of tuning their optical properties upon application of external stimuli. An active tuning of the DBR optical properties can take place through various triggers, but in this work I focused mainly on the electrical and biological ones.

Regard to electrochromic crystals, an attempt was made to create devices whose PBG could be tuned by applying an electric field. In the literature there is a wide range of electrochromic DBRs, whose wide electro-tunability is obtained by immersing the Bragg stack in a liquid electrolyte with the aim of improving the migration of ions and electrons. This leads to a degradation of the samples, limiting the possibilities of their applications. To address this problem, my work has focused on the fabrication of electrolyte-free devices, demonstrating the electro-responsiveness of DBRs without the use of liquid electrolytes. The electro-optical properties of ITO (indium doped tin oxide) were exploited for this purpose. ITO is a plasmonic semiconductor widely used thanks to its low electrical resistivity ( $10^{-4}$   $\Omega$ cm) and large band gap (3.7 - 4.1 eV) which makes it transparent in the visible range. Its carrier density oscillations generate localized surface plasmon resonances (LSPR) in the near infrared (NIR) region, which can be dynamically modulated by applying an electrical bias. The significantly lower charge density, compared to that of bulk

metals ( $10^{21}$  cm<sup>-3</sup> and  $10^{23}$  cm<sup>-3</sup>, respectively), allows large modifications to the LSPR with minimal changes. By applying an electric field to an ITO/TiO<sub>2</sub> DBR, it was possible to investigate the optical response of the device. The results showed a maximum PBG blue shift of 40 nm, in accordance with the predictions of the Drude model. Slow response time (from 10 s to some min.) and an electrical characterization identified the charge injection through impurities/defects as the main cause of ITO doping. A possible concomitant effect could be titania polarization, but the response time would be quick in this case. Two further types of DBR, one compact and one nanoparticles-based, have been manufactured to better investigate the intrinsic properties of the devices. The results showed how in the nanoparticles based DBRs there is an interconnection between the constituent layers due to the presence of different phases and the non-planarity of the films. On the surface of the ITO NPs there is the formation of an accumulation layer due to the application of the electric field, leading to the change of the refractive index. So, the greater the contact area between the two constituent materials the greater the number of electrons that can be injected between the layers and so the greater is the change in the refractive index. This study demonstrated the possibility of fabricating electrochromic PhCs without the aid of liquid electrolytes. Moreover, the devices have been subjected to charge and discharge processes several times, even after a long time from their manufacture, demonstrating their

stability even after long periods and in a not inert storage atmosphere. DBR can be used for bacterial detection. During my work I have also been involved in the fabrication of one dimensional TiO<sub>2</sub>/SiO<sub>2</sub>/Ag DBRs, with the aim of using them as optical sensors for bacterial contamination. Starting from the centuries-old knowledge of the antimicrobial action of silver, the interactions of this material with both Gram-positive (*Micrococcus luteus*) and Gram-negative (*Escherichia coli*) bacteria and the optical response that leads to its implementation in a DBR have been investigated. The results showed that the interaction between the negative charges present on the membrane of the bacteria and the positive charge of the silver ions leads to an endocytosis of the latter by the cell. This partial dissolution of the metal favours a change in the size of the deposited silver layer and, consequently, a change in the plasmonic response of the material. Furthermore, the variation of Ag leads to a substantial modification of the effective refractive index of the entire structure, causing a shift in the photonic band gap and a colorimetric response visible to the naked eye.

## ADVANCED LASER TECHNOLOGIES FOR NOVEL THZ TIME DOMAIN SPECTROSCOPY

Lisa Marta Molteni - Supervisor: Prof. Gianluca Galzerano

Terahertz time-domain spectroscopy is an interesting tool for a large variety of applications such as non-destructive testing and imaging of different samples, biomedical sensing, security and communication.

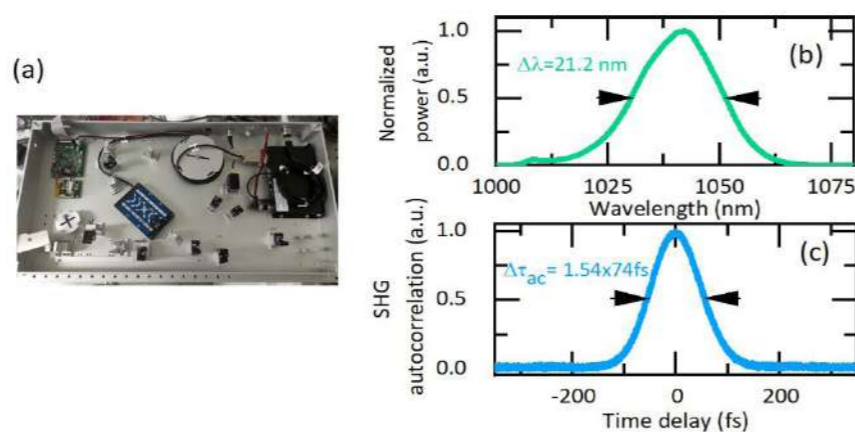
Thanks to the peculiar properties of THz radiation in particular the transparency of many packaging materials such as paper and plastic THz time-domain spectroscopy is nowadays implemented for more industrial related purposes such as quality control testing, food inspections and material identification in chemical, pharmaceutical and medical fields.

The aim of the industrial PhD is the development of an innovative and compact laser sensing system in the THz frequency region especially for black plastics identification and sorting. Plastic is a fundamental material in the production of goods; however, it is difficult to reuse and recycle because of its great variety and the mixing of various polymers. This project is focused on black plastics containing brominated and chlorinated flame retardants that are used in different industrial sectors from electronics to automotive. These types of plastics cannot be recycled and need to be detected and sorted from the recyclable ones. With this specific goal during the PhD research a versatile THz time-domain spectrometer based on photoconductive antenna (PCA) technology and compact ultrafast Yb laser has been developed. The photoconductive antennas offer great advantages for industrial related applications being compact, efficient, and reliable devices that needs low power femtosecond optical radiation

to ensure high quality broadband THz pulses. The first part of the PhD research was therefore devoted to the development of a compact pre-industrial prototype of a diode-pumped ultrafast laser. It is based on a Yb:CaGdAlO<sub>4</sub> active media that can reach a stable mode-locking condition providing ultrafast broadband pulses in the wavelength region of 1040 nm. The pre-industrial prototype was realized in partnership with University of Pavia and the laser company Bright Solutions. Figure 1 shows the picture of the developed laser prototype and the characterization measurements of the spectrum and autocorrelation reporting a bandwidth of almost 20 nm with transform-limited pulse duration of 74 fs with an average output power of 60 mW and a repetition frequency of 160 MHz.

Thanks to the peculiar properties

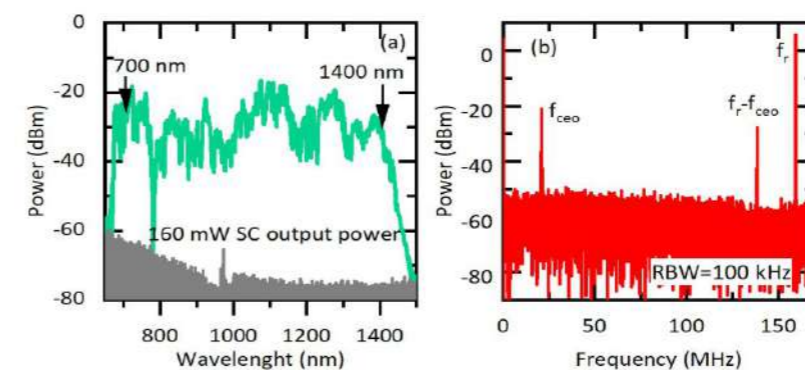
of this solid-state laser in terms of mode-locking stability and low intensity and frequency noises it opens up the possibility to use it also for more scientific related applications. In particular, during the second part of my PhD research activity, this laser source has been exploited for the generation of broadband optical pulses with duration shorter than 20 fs using a compact low-cost nonlinear fiber compressor for nonlinear microscopy, time-domain spectroscopy and optical parameter amplifiers seeding. Moreover, the Yb:CALGO laser prototype has been turned into a low-noise optical frequency comb synthesizer operating in the spectral region between 650 nm to 1500 nm, which is extremely interesting for frequency metrology and broadband precision spectroscopy. Figure 2 reports the octave-spanning supercontinuum spectrum (panel a)



**Fig. 1**  
(a) Yb:CALGO laser pre-industrial prototype, (b) optical spectrum and (c) autocorrelation characterization measurements of the laser pulses.

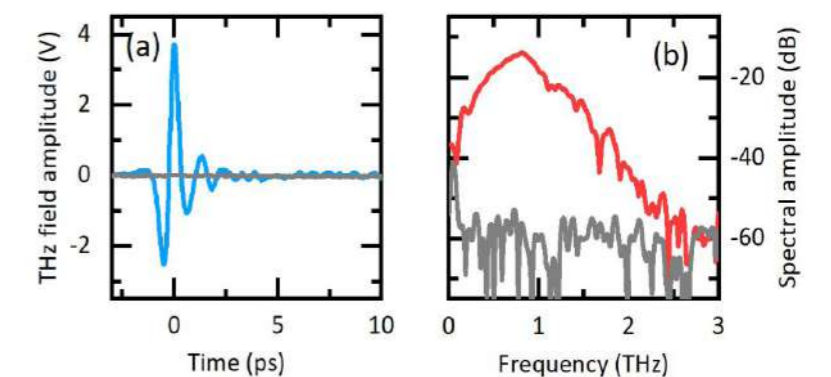
and the radio frequency spectrum detected at the output of the f-2f interferometer (panel b) showing the carrier envelope offset frequency of the Yb:CALGO comb.

The final part of the PhD activity has been devoted to the realization of the THz time-domain spectrometer exploiting the Yb:CALGO ultrafast laser prototype and two fiber-coupled low-temperature growth InGaAs PCAs. This instrument operates in the spectral region between 0.2 and 2.5 THz and can reach a minimum single scan acquisition time of 100 ms, satisfying the industrial requirement of fast measurements. The measured THz electric field as a function of time and the corresponding calculated spectra, performed with the optical sampling by cavity tuning technique (OSCAT), are presented in figure 3. To prove the capabilities of the proposed THz time-domain spectrometer, in the PhD thesis are also reported



**Fig. 2**  
(a) Yb:CALGO optical frequency comb octave spanning supercontinuum spectrum, (b) Radio frequency spectral measure of the f-2f interferometer beat note detecting the CEO frequency.

several measurements of the spectral transmittance of some black plastic samples and of some semiconductors (GaP, AsGa, Si) together with their retrieved refractive indexes and absorptions.



**Fig. 3**  
Measured THz time domain traces (a) and the corresponding calculated spectral amplitude (b) using the OSCAT technique.

# ATTOSECOND TRANSIENT REFLECTION SPECTROSCOPY FOR ULTRAFAST ELECTRON DYNAMICS: EXPERIMENTAL INVESTIGATION AND THEORETICAL METHODS

Bruno Moio – Supervisor: Mauro Nisoli

The quest for technologies which can circumvent the current limitations of electronics has pushed the scientific community towards the study of new and exotic physical systems. In the last decades the availability of intense light sources, delivering short laser pulses, paved the way to the investigation of novel technological fields, where electronics and optics coexist. This opened the path towards the development of innovative devices with improved performances. In particular, the availability of tabletop light sources in the infrared (IR) and extreme ultraviolet (XUV) spectral range, characterized by extremely short duration in the sub-femtosecond range, allowed the flourishing of experimental frameworks previously unseen, able to assess the electron dynamics in molecular and solid-state systems, with unprecedented resolution.

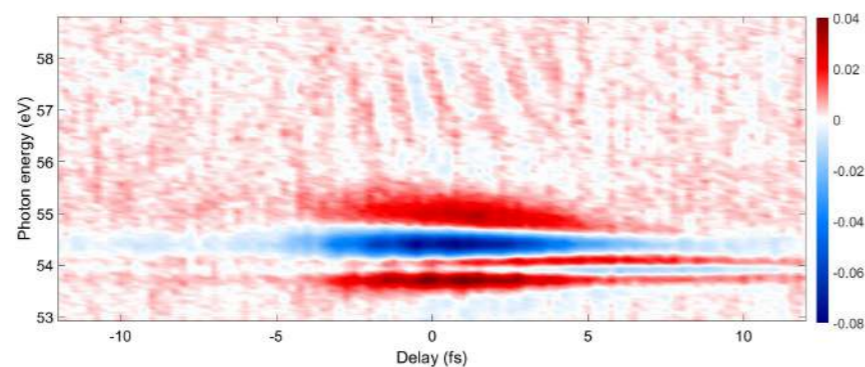
In these regards, Attosecond Transient Reflectance Spectroscopy (ATRS) has proved a valuable tool for assessing the innermost electron dynamics in solids, while circumventing the limitations of other techniques. It allows to employ bulky samples, which are more robust and can therefore withstand higher intensities, thus opening the way for the investigation of several materials in the strong-field regime. We employed ATRS for the assessment of different kinds of electron dynamics in various materials. We used it to investigate the ultrafast response of the core exciton in magnesium fluoride (MgF<sub>2</sub>), where we observed for the very first time in the literature that the exciton exhibits a dual nature, both solid and

atomic-like. The former is responsible for the optical Stark effect the exciton undergoes, while the latter shows up in the dynamical Franz-Keldysh effect (DFKE). It is worth mentioning that the DFKE has never been observed before for these physical systems, and that its tunability, that we proved theoretically, is a promising candidate for the future development of ultrafast opto-electronics.

We also employed ATRS for the investigation of the ultrafast all-solid response of germanium, where we observed for the first time the interplay between the inter- and intra-band electron motion with unprecedented temporal resolution, and of diamond, where we investigated the DFKE in an energy range that for long time had remained inaccessible.

Regarding the investigation of core-exciton dynamics, an important

limitation to their precise assessment is the lack of an efficient and simple tool for a theoretical description of the physical processes behind. For a long time the only feasible way was to use complicated ab initio calculations to get a theoretical description of the investigated systems, while limiting the versatility of the experimental framework. While this description may be very precise, a simple and intuitive picture of the physical phenomena that drives the observations is impossible. For this, we developed a novel approach for the extraction of the relevant parameters describing the core-exciton dynamical response out of a transient reflectance trace. The technique, called ePIX (extended Ptychographic Iterative engine for eXcitons), is based on the ptychographic iterative engine widely used in the field for the simultaneous characterization of the XUV and IR pulses in a two-color photoelectron experiment. The method can recover



**Fig. 1** Transient reflectance trace of magnesium fluoride, showing a slow signal related to the core-exciton state decay, and a sub-fs ultrafast oscillation.

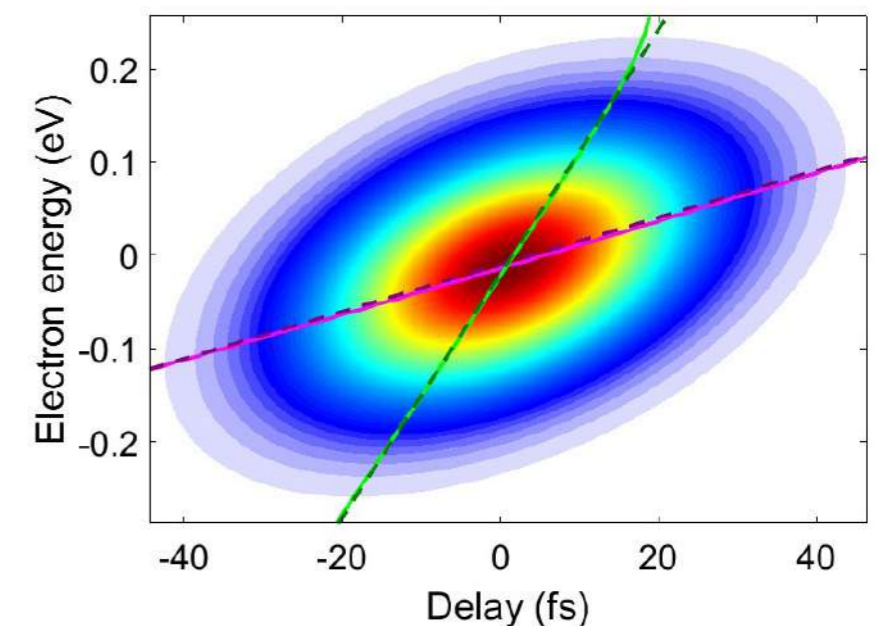
both the exciton dynamics, in the form of the real-time dipole moment of the excitonic state, and the IR pulse that drives the dynamics out of equilibrium. The advantage of our technique is that it requires no prior information on the dynamical response, unlike other available methods, while showing great precision and accuracy in the reconstruction, even in the cases where the dynamical response has a duration that compares to the duration of the probe.

Another important issue for the experimental framework mentioned above is that the availability of pulses with a shorter and shorter duration, in the XUV spectral range, is very demanding for their characterization. This is indeed a quite challenging task and in the past has fostered the development of several characterization methods. However, the need for good performances and a precise characterization, beyond the intrinsic limitations of the detection devices, calls for a deeper comprehension of the physical processes the characterization methods are based on. For this reason we developed a simplified model for the description of the two-color photoemission, allowing to get better physical insights on this phenomenon. We used the simplified model to bind the geometrical properties of the photoemission traces to the temporal characteristics of the pulses involved, for example showing that in the case of single-harmonic XUV radiation the resulting trace resembles a time-frequency distribution of the pulses, de facto extending all the tools for

signal analysis to the field of pulse characterization. In particular, we showed that it is possible to directly assess the dispersion of the pulses, without employing complicated iterative characterization methods.

On the other hand, we used the simplified method to develop STRIPE (Simplified Trace Reconstruction In a Perturbative rEgime), a novel method for pulse characterization, which is faster than other available tools but equally reliable. We proved that our method can be used in any available experimental regime (RABBITT,

Streaking, etc.) and that it shows an extreme robustness against the noise and all signal non-idealities that affect the measurements, proving as a valuable tool for applications to real experimental cases.



**Fig. 2** Upper sideband extracted from a single-harmonic spectrogram. The lines show the tilt functions, as geometrically extracted from the sideband (solid) and computed from the pulses temporal parameters (dashed).



# GROUP-IV TELLURIDES AS A PLAYGROUND FOR ENHANCED PERFORMANCES IN SPIN AND ANGULAR RESOLVED PHOTOEMISSION SPECTROSCOPY

Luca Nessi – Supervisor: Matteo Cantoni

The boost received in the last twenty years by the development of new technologies in governing thin films depositions, tailoring new compounds and scaling down to the monolayer limit of two-dimensional (2D) materials, opened new horizons both for computing and storage technologies. Among the several options offered by modern condensed matter physics, the intriguing properties of electrons spin triggered a still increasing field of research which is called spintronics, namely spin-electronics. The idea of involving both charge and spin in the processing of information has completely changed the paradigms in conceiving memory elements (the discovery of giant magnetoresistance brought the Nobel Prize in Physics in 2007 to Fert and Grünberg). This very active field of research is rapidly passing from spintronics to spin-

orbitronics, where the electron spin is exploited in strict relation with the electron orbital motion. This new field has intensified its interest in materials with strong spin-orbit coupling, glimpsing the possibility to engineer them by integrating conventional electronics with spin functionalities. Two challenging proposals are under investigation nowadays. The former deals with the replacement of magnetic fields in writing information in magnetic memories (which suffer of scaling and relative slow operations) via current-induced spin torques produced by injecting a spin current into a ferromagnetic material, moving to fully electrical-controlled systems. From the computing perspective, the idea consists in the replacement of CMOS technology with a scalable spintronic logic device technology that operates via spin-orbit transduction for an all-in-one

platform with enhanced performances in terms of scalability and energy consumptions. This could pave the way to exploit such a technology in classical von Neumann computer, as well as in new computing paradigms such as neuromorphic devices for artificial intelligence applications, as proposed by Intel in 2019. In the framework of these challenges, several materials were proposed, from heavy metals to multi-functional oxides, to topological materials. This thesis deals with a new class of compounds, namely ferroelectric Rashba semiconductors (FERSC) (figure 1a), strongly promising for formerly mentioned applications. This class of materials was discovered in 2013 with GeTe as a father compound and it soon became object of an investigation which spans from material science fundamental perspective to a very applicative field, in which they are raised to new materials for beyond-CMOS computing.

This thesis covers two different topics. From the fundamental physics perspective, the study of a relative new member of FERSC family is proposed. SnTe is a topological crystalline insulator (TCI) and, in the 2D limit, it is ferroelectric. During this work, a band structure engineering to tune SnTe properties from TCI to FERSC and allowing the coexistence of these two phases was performed exploiting doping with germanium. The alloy GeSnTe was grown in the form of thin films (few nanometers, preserving a bulk identity) and characterised by means of synchrotron radiation with spin- and angle-resolved

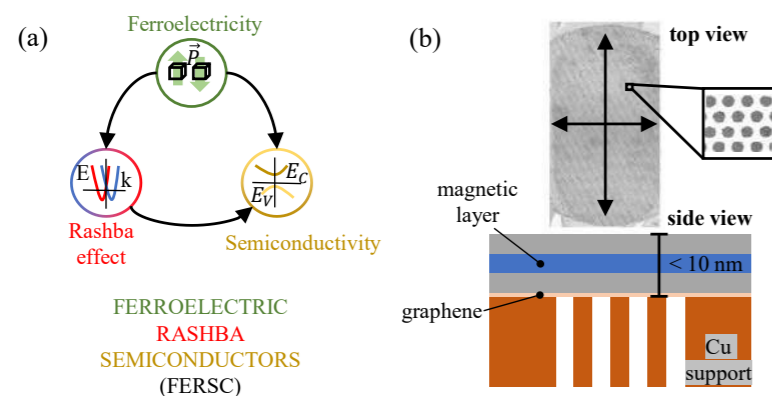
photoemission spectroscopy (SARPES). Together with a comparison with theoretical calculations, a certain concentration of germanium allows to reach an intermediate state which displays both Rashba effect and ferroelectricity at room temperature, signatures of FERSC and topological states, resembling the TCI behaviour of bare SnTe. This represents a very important achievement and could be of potential breakthrough in spin-orbitronics application.

The second topic faced in this work is strictly related to the technique employed for the characterisation described above. SARPES represents one of the most important tools used to obtain a full picture of the electronic band structure of materials, together with their spin character. The spin degree of freedom is of paramount importance in many classes of materials. The state-of-art technology for SARPES is based on very low energy electron diffraction (VLEED) detectors. The photoemitted electron is selected in energy and momentum and scattered by a ferromagnetic (FM) target. The relative direction between spin and magnetisation vector of the FM material influences the efficiency of the process and makes the distinction between spin up and spin down electrons possible. This type of measurement suffers of very long integration times because the energy-momentum space is scanned pointwise.

In this thesis a radically new way of detection is proposed, based on idea conceived in 2017, relying on spin filtering through free-standing magnetic membranes. In particular,

the selective transmission of electrons through a FM is exploited to detect their spins. The realisation of such devices was performed depositing nanometric FM films (to have a reasonable electron transmission) on top of free-standing graphene ultrathin films (2 to 8 monolayers) stacked into a 2D matrix of micrometric pixels (figure 1b). The engineering of the heterostructures made possible to have a sufficiently large robustness together with the tuning of the magnetisation direction, in-plane or out-of-plane, to achieve a 3D reconstruction of the spin degree of freedom. The samples were characterised from the mechanical and magnetic points of view, testing the influence of the number of graphene monolayers on their robustness and employing different deposition techniques. A rate of 94% of intact membranes was measured and in-plane and out-of-plane magnetic anisotropies were obtained by means of different heterostructures based on Co and CoFeB. A non-zero remanence magnetisation and a coercive magnetic field of 3 mT were measured by Faraday effect. They are sufficiently larger to guarantee the stability of the magnetisation during a hypothetical measurement. Finally, a spin gun set-up was optimised and employed to characterise the transmission spin filtering properties of such devices. The realisation of this 2D matrix represents a proof-of-concept of a reliable workflow which provides a system of free-standing magnetic films which could be employed in spin polarimetry, strongly reducing the measurement time. The industrial

realisation of this prototype could represent a turning point in SARPES since the exponentially increasing interest in the investigation of new materials.



**Fig. 1**  
**(a) Ferroelectric Rashba semiconductors main properties; (b) top and side views of the prototype device based on free-standing magnetic membranes on graphene for the realisation of a 2D spin detector.**

# FEMTOSECOND LASER WRITING OF INTEGRATED PHOTONIC CIRCUITS FOR QUANTUM TECHNOLOGIES

Simone Piacentini – Supervisor: Roberto Osellame

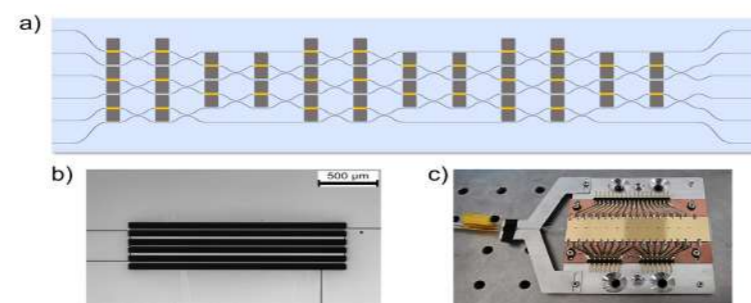
The counterintuitive laws of quantum mechanics promise to be at the basis of a tremendous technological improvement, the so-called Second Quantum Revolution. As a matter of fact, the exploitation of purely quantum phenomena such as quantum superposition, entanglement, and teleportation, will enable faster and more complex computations, secure communications, and measurements with enhanced sensitivity. However, there are some problems that researchers need to address to achieve useful implementations. For instance, quantum states are quite fragile, and even the slightest interaction with the environment could affect them. Moreover, to achieve a useful operation, it will be necessary to generate and manipulate thousands or even millions of quantum states in the same system, therefore scalability is another issue to address. Among the main platforms that have been proposed for the development of quantum technologies, quantum photonics is one of the most promising. Photons are indeed robust to noise and unwanted interactions with the surrounding, thus requiring less strict error protection techniques. Moreover, they are well-suited for fast and efficient communications, and can be easily manipulated with linear optical elements such as beam splitters and delay lines. Regarding the scalability issue, quantum photonics could benefit from the expertise acquired in the last years in the development of integrated photonic circuits, which would provide the miniaturization and the interferometric stability required in useful quantum devices. In this respect, among the possible fabrication platforms, femtosecond

laser writing (FLW) of waveguides in glass is probably one of the most versatile. This technique exploits the nonlinear interaction between a focused femtosecond laser and a transparent substrate to induce a localized increase of the refractive index of the bulk material, thus enabling the direct inscription of integrated optical waveguides by simply translating the sample in the three dimensions. With respect to other fabrication platforms, FLW provides fast prototyping capabilities and does not require clean room facilities, being the processing of the bulk substrate less sensitive to its surface cleanliness. Moreover, since the material modification is limited to the focal spot and its immediate surrounding, it is possible to inscribe circuits with unique 3D geometries. The low induced refractive index contrast, of the order of  $10^{-3}$ , enables an optimum interfacing with optical fibers, without the need of lossy grating couplers. Despite its main limitations, which are the low miniaturization

capability and the sequentiality of the fabrication process, FLW can be very useful in the current quantum photonics research, where achieving proofs-of-concept and intermediate results is very important. In this thesis work we present the implementation by femtosecond laser writing of several integrated circuits, useful in different fields of quantum technologies. First, we show that FLW could be a valuable platform for satellite-based optical quantum communications. In particular, by replicating the typical conditions that an instrumentation in a satellite would experience in a space mission, including the exposure to charged particles and high-energy radiation, high vacuum and temperature variations, we demonstrate that femtosecond laser written passive photonic circuits could withstand such a harsh environment without any degradation of their operation. The second topic of this thesis is focused instead on the implementation of two photonic circuits for scalable quantum information processing. In this regard,

the first device is a low-loss and low-power six-modes universal photonic processor. The reconfigurability required for its universality is achieved by means of a mesh of 15 Mach-Zehnder interferometers (MZIs), whose internal and external phases can be controlled by 30 thermal phase shifters fabricated between isolation structures for reducing both their thermal crosstalk and their power consumption. After a proper characterization with classical light, we show that the inscribed circuit can implement any arbitrary unitary transformation with state-of-the-art fidelity and losses. Concerning the second circuit, we exploit instead the unique 3D capability of FLW for implementing a 32-modes interferometer based on a continuously coupled 3D waveguide array, which can be reconfigured by controlling 16 phase shifters to perform a boson sampling experiment with up to four single photons. In this respect, one of the main limitations for achieving a scalable photonic platform is represented by the low efficiency of single photon sources. Therefore, in this thesis work we also show the characterization and optimization of the emission of semiconductor quantum dots with high brightness, purity, and indistinguishability, which are for this reason among the most promising single photon sources. In particular, this activity was performed during a period as a visiting student at the University of Vienna. We then present the femtosecond laser writing of the first quantum photonic memristor, a device composed by an MZI whose internal phase is controlled by a feedback loop based on the measurement of its output. By injecting in the device an

arbitrary entangled photonic state, and by performing a tomography on its output, we show that the MZI reflectivity presents a hysteretic behavior which preserves the quantum coherence of the input states, and therefore could be exploited for the implementation of the nonlinear connections required in a photonic quantum neuromorphic network. As a last topic, we present the inscription of a four-arms interferometer, the four-modes equivalent of an MZI. Notably, this device would enable the simultaneous quantum estimation of three optical phases with an enhanced sensitivity if compared to a classical measurement, thus finding applications in the field of photonic quantum metrology.



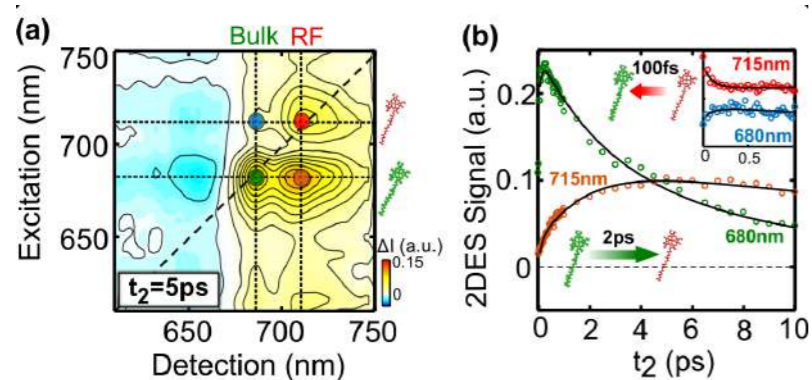
**Fig. 1**  
**ix-mode photonic processor. a) Scheme of the optical circuit, with the phase shifters in gold and the isolation structures in grey. b) Microscope image of the isolation structures. c) Picture of the assembled device.**

# LIGHT-DRIVEN ENERGY CONVERSION PROCESSES IN NATURAL AND BIO-INSPIRED LIGHT HARVESTING SYSTEMS PROBED BY TWO-DIMENSIONAL ELECTRONIC SPECTROSCOPY

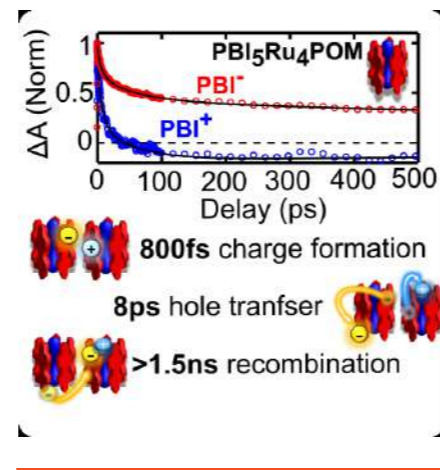
Mattia Russo - Supervisor: Giulio Cerullo

In recent years the generation of renewable energy from bio-inspired systems came into the spotlight, with the goal to mimic the efficient energy conversion mechanism performed by natural organisms as higher plants, cyanobacteria and algae. Such systems exploit chromophores as chlorophylls (Chls) and carotenoids located in peripheral antenna complexes to capture the solar energy and transfer it to a pigment-protein complex, called reaction center (RC), in which charge separation and the subsequent photosynthesis chemical reaction take place. All these excitation energy transfer (EET) processes occur on an ultrafast timescale and their study is of crucial importance in order to, on the one hand, to understand natural photosynthesis and on the other hand derive design rules for artificial light-harvesting complexes. In order to temporally and spectrally characterize the EET processes, a combination of

high temporal and spectral resolution is required. The two-dimensional electronic spectroscopy (2DES) technique is well suited for this aim since it generates time-resolved 2D correlation excitation/detection frequency maps typically with sub20-fs time resolution. Briefly, 2DES exploits the interaction with three delayed laser pulses to generate the emission of a third-order nonlinear optical signal from the sample. The first and the second pulse act as a pump and the delay between them is called coherence time ( $t_1$ ). The third pulse acts as a probe and it is delayed by  $t_2$  (waiting time) with respect to the second pump. The signal generated after the probe is spectrally resolved by a spectrometer to obtain the detection frequency. The nonlinear signal is then Fourier transformed along the  $t_1$  axis to generate the excitation frequency and obtain 2D excitation/detection maps as a function of  $t_2$ . In the first part of this work, we



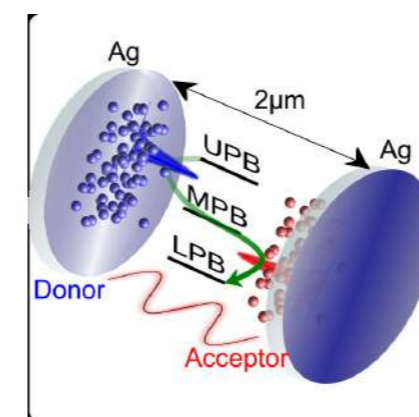
**Fig. 1**  
(a) 2D map at  $t_2=5ps$  of *Spirulina Platensis*; (b)  $t_2$  traces of the diagonal and cross peaks indicated in panel (a)



**Fig. 2**  
PBI+ and PBI- dynamics with temporal characterization of the mechanisms

adopted 2DES to characterize the EET mechanism in natural photosystems in which Chls red forms (RF), absorbing at wavelengths longer than 700 nm, are involved; specifically, we study photosystem I (PSI) in cyanobacteria and higher plants. Fig. 1a shows the 2D map of cyanobacterium *Spirulina platensis* at  $t_2=5ps$ . The peaks along the diagonal reflect the static absorption peaks of the so-called “bulk” Chls, that mostly surround the photosystem I (PSI) at 680nm (green circle) and the peaks of the Chls RF at 715nm (red circle). The cross peaks (blue and orange circles) indicate EET processes within the two species. Fig. 1b shows the dynamics of the four peaks and the associated mechanisms. By exciting at 680nm, the energy is transferred from the bulk (green curve) to Chls RF (orange curve) in 2ps, a process usually referred as a downhill EET. By exciting at 715nm (dynamics are shown in the

inset), part of the energy absorbed by Chls RF is transferred back to the bulk in 100fs, giving rise to an uphill EET. The same processes with similar time scales are observed also for the PSI in higher plants, but its different conformation produces a slower relaxation to the ground state. These results show the efficiency of the EET processes among Chls and demonstrate that Chls RF participate to the photosynthesis chemical reaction. In natural systems, there are some aspects as fast charge recombination and spatially limited EET that make the system unoptimized. The first aspect drastically reduces the effective fuel yield obtained from the photosynthesis chemical reaction. In this view, bio-inspired photosystems that mimic the structure of the natural one, are synthesized to increase the recombination time from the ps to the ns time scale. Here we report



**Fig. 3**  
Organic microcavity scheme including polaritons states that assist EET between donor and acceptor

an ultrafast spectroscopy study of the so-called “quantasome” system, that uses Perylene Bisimide (PBI) as light harvesting antenna and a Ruthenium Polyoxometalate (Ru4POM) as a catalytic cofactor. Following photoexcitation of PBI, ultrafast charge separation leads to the generation of charges in the antenna (PBI+ and PBI-). Fig. 2 shows the dynamics of the PBI anion (red) and cation (blue) following photoexcitation. The two species show a common dynamic till 800fs, in which the formation and consequent localization of the charges take place. The 8ps time constant represents the hole transfer from PBI+ to Ru4POM+. The third time constant reveals a recombination time longer than 1.5ns that demonstrates a long-lived charge separation. The other aspect that can be improved for the production of innovative light harvesting devices is the distance at which EET between molecules can take place, beyond the typical limit set by the Förster radius (10nm). To this aim, we study possible EET between donor/acceptor molecules spatially separated by  $2\mu m$  with spectrally separated excitonic states. This long range EET can be achieved when the two molecules are confined in an optical microcavity if both excitonic states are strongly coupled with the same cavity mode. This regime promotes the formation of three hybrid polaritons states, named upper polariton branch (UPB), middle polariton branch (MPB) and lower polariton branch (LPB). Fig. 3 shows the scheme of the microcavity under study and the energy levels of the system. 2DES enabled us to observe that the

EET process between molecules is assisted by polaritons states and that the MPB works as a bridge between them.

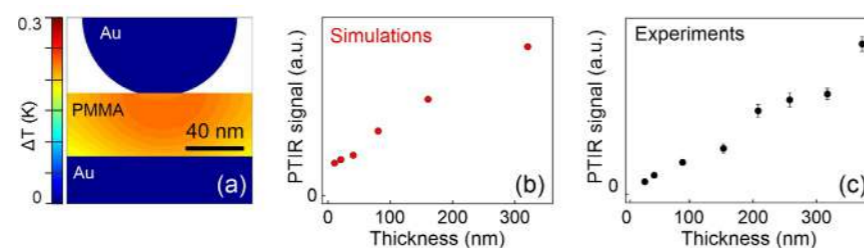


Francesco Rusconi – Supervisor: Paolo Biagioni

Infrared (IR) radiation plays a crucial role in the investigation of the basic constituents of matter, since it can excite molecular vibrations. The importance of IR spectroscopy stems from the fact that the spectral features arising from molecular vibrations represent a distinctive label for the sample under study. However, for some applications, the information coming from traditional spectroscopic IR techniques is either hard to obtain (i.e., the signals are too weak) or difficult to understand. These limitations might be circumvented by employing nanostructured systems, properly tailored to sustain electromagnetic resonances, through which it is possible to create and exploit highly enhanced and tightly confined fields. Thanks to the resonant behaviour of these fields, we are able to selectively detect molecules with specific spectral features. This approach represents the basis of well-developed fields of study, such as surface-enhanced spectroscopy or biosensing. In this context, I focused my Ph.D. activity on two advanced applications of enhanced spectroscopic techniques in the IR. The first case I investigated is the photothermal induced resonance (PTIR) technique. In this technique, an atomic force microscope (AFM) tip scans a sample (typically a thin film) which is illuminated by infrared light. The light wavelength is tuned to an absorption line of the material, which resonantly absorbs the impinging optical power. This leads to heating and to a consequent thermal expansion, which is detected by the AFM tip. By spanning the wavelength of the light

and scanning the sample with the AFM tip, it is possible to produce a chemical mapping of the surface. In this technique, the enhancement is given by the resonant illumination paired with the confinement of the tip, which grants subwavelength resolution. Since PTIR is a novel technique, there is no solid theoretical background yet providing a rationale to interpret the experimental results. To improve our understanding of the mechanisms responsible of the PTIR signal, we consider a robust set of experimental data, collected as a function of the sample thickness. Then we model both the optical absorption and the heat transfer by employing finite-difference and finite-element simulations. In this way we could evidence the importance of the thermal resistances at the interfaces of the film in interaction with the AFM tip, which govern the heat transfer at the scale we are considering. In the end, our work gives a guideline to understand the PTIR signals, weighting on different so far overlooked contributions and explaining

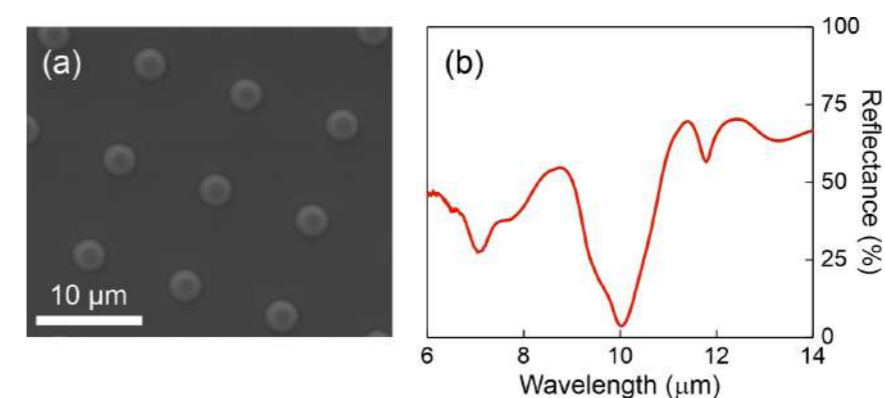
a counterintuitive linear dependence on the film thickness (Fig. 1). The second case I treated is the design, fabrication and characterization of a dielectric sensor working in the mid-infrared (MIR). The aim was to create a platform exhibiting resonances with a high and confined field enhancement. The typical nanostructures used to meet these requirements are nanoantennas made from noble metals, i.e. plasmonic nanoantennas. However, metals are intrinsically affected by ohmic losses, which limit the quality of the resonances. In the last years, dielectric antennas have been proposed as an alternative to plasmonic ones to realize low-loss platforms. Dielectric resonances have already been exploited for several applications in the visible and near-infrared. However, their extension to the MIR is not straightforward. In particular, the materials of choice for the fabrication of semiconducting antennas operating in the MIR and those employed as substrates typically have similar refractive indices in this



**Fig. 1**  
**(a) Representative temperature distribution in a PTIR experiment. Simulated (b) and experimental (c) dependence of the PTIR signal on the sample's thickness.**

spectral range. This is an adverse configuration for the establishment of strong resonances, which cannot be obtained without a strong index contrast between the antenna and the substrate. As a solution to this problem, we employ a highly-doped semiconductor layer as the substrate. By controlling the doping, we are able to tune the real part of the permittivity of this layer to have a zero-crossing at the desired resonance frequency of the antenna, realizing the epsilon-near-zero condition (ENZ) and, consequently, a strong discontinuity between the refraction index of the antennas and of the substrate supporting them. With this further degree of freedom, we can tailor the optical properties of the substrate to obtain sharp antenna resonances. Following these guidelines, we have designed a double array of InAs nanoantennas on top of an ENZ substrate. We fabricated the platform

via electron-beam lithography and characterized it with reflectance spectroscopy, in which we observe a sharp resonance in the MIR (Fig. 2). The demonstration of a dielectric platform working in the MIR confirms that such devices represent a valid alternative to the plasmonic ones, which are limited by ohmic losses, opening the way to a wide range of advanced spectroscopic applications.



**Fig. 2**  
**(a) Scanning electron microscope image of the fabricated nanoantennas. (b) Reflectance spectrum of the double array, showing a MIR resonance around 10 μm wavelength.**

## OPTOFLUIDIC BIOCHIPS FOR SINGLE-CELLS IMAGING FABRICATED WITH FEMTOSECOND LASER MICROMACHINING

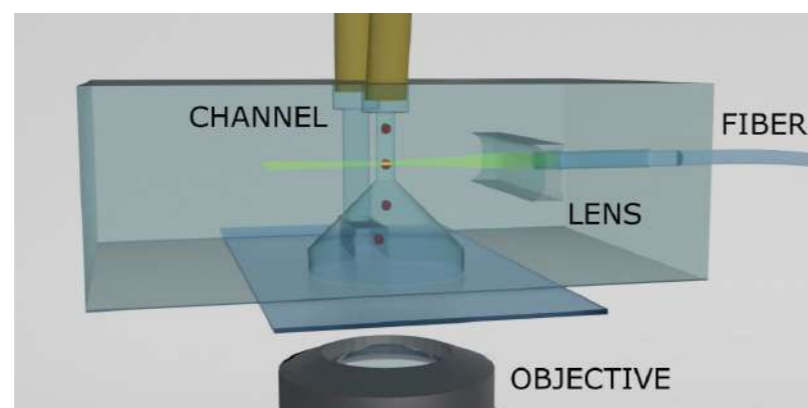
Federico Sala - Supervisor: Roberto Osellame

The concepts of Lab-on-a-Chip (LOC) and micro Total Analysis System ( $\mu$ TAS) date back to twenties years ago, when life scientists and chemists started to raise the interest in performing analysis on miniaturized (fluidic) systems in order to improve the performances and reduce the time duration of their experiments. Since then, the concept of microfluidics, biochips and integrated systems strongly developed in many fields, from chemistry to biology, from energy science to drugs development. In particular life science strongly benefited from the development of LOC and from the integration of microfluidic circuits, that acts as a backbone of the devices, with many analysis techniques, like chemical, electrical, magnetic or optical detection.

In the last years, LOCs found a new specific field of application in the analysis of single cells. In the last decades several studies proved that the behavior of a cellular population is not always related to its composition. Indeed, the average behavior of a cellular population can be misleading and can hide the presence of a sub-population of interests, like it happens in the case of heterogeneity in cancer cells. For this reason, in the last years the interest in single-cell analysis strongly increased. Microfluidic provides a convenient and precise way to handle and deliver single-cells, ensuring at the same time a liquid environment that could mimic "real life" conditions. At the same time, many optical techniques used to study cell in suspension can be integrated in the same LOC, starting from standard microscopy to more

complex analysis systems that use light as an active probe, like optical tweezers. Furthermore, the use of LOCs allows the study of single-cells with high resolution, high sensitivity, probing each cell one-by-one and it can provide a big amount of data, useful for statistical analysis of populations and sub-populations. In the end, optofluidic-based LOCs present themselves as a clever and specific tool that could empower biologists' and life scientists' analysis capabilities, providing at the same time a compact and user-friendly system that could be approached by not-specialized operators. As the technique developed during the last two decades, also the technologies employed to realized LOCs strongly improved. Out of those, Femtosecond Laser Micromachining (FLM) is a direct laser writing technique that allows the realization of 3D microfluidic, micromechanical and optical components on the same glass

substrate, allowing the realization of complex, biocompatible, monolithic and fully integrated Lab-on-Chips. The structures are realized by moving the laser beam inside the pristine substrate, thus the design can be changed and adjusted straightforwardly, allowing fast and cost-effective prototyping. This technique has been used in the last year to realize state-of-the-art optofluidic devices, employed in biology and single-cell research. My work focused on the realization of four different optofluidic platforms used for the study of different types of single-cells. They present both fluidic components, optical components (e.g. microlenses) and photonic circuits, based on integrated waveguides. All these elements have been realized on glass fully exploiting the possibilities offered by FLM technique. The first device is a LOC system used to perform light-sheet fluorescence microscopy on cancer single-cells. The



**Fig. 1**  
Scheme of light-sheet fluorescence microscope-on-chip device

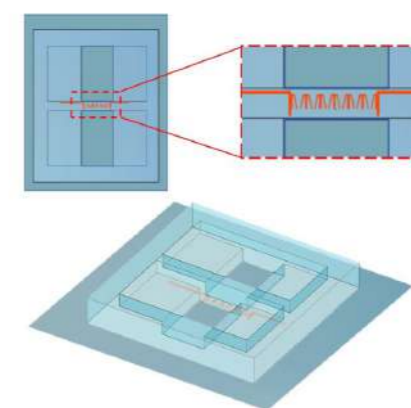
device, reported in Figure 1, consists in a microfluidic channel tailored to the dimension of the specific sample, with an integrated microlens, used to shape the excitation laser beam into a light-plane. While the cells flow inside the microchannel, they pass through the light-sheet and their fluorescence signal is acquired, allowing high throughput and 3D reconstruction.

The second device consists in an improved version of the first one, where the illumination is substituted by two light-sheets, interfering inside the detection microchannel, in order to create a 1D modulated lattice. This illumination, obtained with integrated photonic circuit and micro-lenses, can be moved across the detection plane and it is exploited to perform Lattice based Structured Illumination Microscopy. This device is able to improve the detection resolution along one direction, below the standard resolution of the system and it is a first example of super-resolved acquisition of suspended cells on a totally integrated optofluidic device.

The third biochip consists in a glass-polymer platform for cell migration study and it is schematically reported in Figure 2. It is made of two chambers connected by a series of micrometric funnel constrictions, with dimension smaller than cellular diameter. While the cell migrates from the first chamber to the second one, it is possible to study how they change their shape and configuration to squeeze through the constrictions. Thanks to FLM capabilities, I realized several versions of this device, with different shapes and dimension of the funnels, to tailor the

device on the specific cell line under analysis. These devices were used to study migration behavior of different cells, from the epithelial to the tumoral ones.

Lastly, the fourth device consists in an optofluidic chip with integrated microchannel and photonic waveguides, used to screen the population of single-cell microalgae. This device will act as a core of an automated floating platform installed on the lake of Geneva. It will be used to study the seasonality of the bloom of different phytoplankton species and investigate the status of the lake, from the point of view of the pollution and water quality.



**Fig. 2**  
Scheme of LOC device for single cell motility analysis. The micro-constrictions of the migration area are reported in the inset, in orange.

## EDIBLE ORGANIC TRANSISTORS AND CIRCUITS OPERATING AT LOW VOLTAGE

Alina Sharova – Supervisor: Mario Caironi

Sustainable harnessing of natural resources is key moving towards a new-generation electronics, which features a unique combination of electronic functionality, low cost, and absence of environmental and health hazards. Within this framework, the idea of making electronics edible is a radical approach aiming at offering new opportunities for biomedicine, pharmaceuticals, and food industry. This emerging field envisions electronic edible devices and systems that are intended to be safely ingested, and undergo degradation within the body, digested or metabolized, after accomplishing their task. The unique feature of edible electronics lies in exploiting edible materials of different nature (e.g., food, drugs, vitamins, edible metals, edible pigments, dyes and polymers) as electronics constituents, according to

their electronic properties, to provide all the necessary functional materials: conductors, insulators, semiconductors. Edible electronics foresees a complex future edible system gathering all the essential electronic elements for the acquisition, elaboration, and transmission of the data. The fundamental building blocks for such system incorporate functional active/passive elements and circuits, sensors, power supplies, and communication strategies.

The main focus of this dissertation is placed specifically on edible transistors and circuits as fundamental components to be developed, since they can provide computation and control functionalities. Furthermore, these microelectronic components are among the most complex functional elements to be integrated in the future edible system, from both the materials

and device fabrication point of view. Importantly, owing to the edible nature of power supplies, the requirement of low voltage operation of the transistors and circuits has to be addressed accordingly. Considering the novelty of edible electronics and challenges the field is facing at the moment from the materials and processing points of view, the path towards realization of such devices is not straightforward and requires the scientific and technical efforts throughout all the stages. Therefore, the research activities of this thesis address all the critical steps of the devices' realization starting from materials selection, synthesis and optimization to design, fabrication, and characterization of the final devices. Dielectrics largely control the transistors operational voltage, and often constitute the major volume of the final system along with substrates. Yet, to date, among the explored number of edible dielectrics employed in organic transistors, there are only scarce examples of electrolytic food-based materials used as a gating media able to provide beneficial low-voltage operation of the device at ambient conditions. In this context, we propose a cost-effective and intrinsically edible substance, honey, to be used as electrolytic gate viscous dielectric in organic honey gated field-effect transistors (HGOFETs). Both n- and p-type HGOFETs are demonstrated, with distinctive features such as low voltage (< 1V) operation, long-term shelf life and operation stability in air. The devices are compatible with large-area fabrication processes, such as inkjet printing, on edible tattoo-paper, and can be conformally adhered to different surfaces, in particular,

skin or food items (Figure 1a). Such complementary devices enable robust honey-based integrated logic circuits, here exemplified by inverting logic gates and ring oscillators. A marked device responsivity to humidity provides promising opportunities for sensing applications, specifically, for moisture control of dried or dehydrated food. With the aim to target large-area, scalable, solution-processable and cost-effective edible electronics with improved resolution, we further advance in the development of edible transistors and circuits, and investigate inkjet-printing as a primary patterning technique for edible electrodes. The conducting electrodes represent one of the most abundant components in the device, and their quality and resolution are of particular importance for edible transistors and circuits. Within this framework, gold is proposed as an electrode material of choice owing to its edibility, biological inertness, high electrical conductivity, chemical stability, and proven biocompatibility. The optimization of inkjet-printing process of the commercial water-based gold ink is demonstrated along with a morphological, structural and electrical characterization of the final scalable electrodes. Fully printed water-gated field effect transistors (WGOFETs) are realized in order to assess the quality of the electrodes. The obtained results suggest that inkjet-printed gold electrodes represent the appealing platform not only for edible electronics, but also other areas of research, such as organic bioelectronics. We then demonstrate the versatility of inkjet-printed gold electrodes with fabrication of the electrolyte-gated transistors on various edible

substrates. Considering that some practical applications might require mechanical robustness of the devices in combination with their low-voltage operation, the use of solid-state electrolytes as a gating media is of high interest. In this context, we propose chitosan, an edible and nutritive polysaccharide, mainly obtained from shrimp and crab shells, to be used as a solid-state electrolytic gate dielectric in fully printed chitosan-gated transistors. Fully printed chitosan-gated complementary n- and p-type transistors and logic circuits, namely, inverting logic gates, operating at low voltages, <1 V, are demonstrated on flexible edible ethylcellulose substrates. The devices feature long-term shelf life and operation stability in ambient air, and can be integrated into various edible items, in particular, pharmaceutical capsules (Figure 1b). Ultimately, having developed a platform for edible transistors and circuits, we focus on the least investigated class of materials towards edibility, semiconductors. Specifically, we explore the potential of employing copper phthalocyanine, a cosmetic blue pigment found in toothpastes, as a semiconductor for the development of the fully edible electrolyte-gated devices.



**Fig. 1**  
**Digital photograph of a) HGOFETs on flexible edible tattoo-paper substrate, transferred onto an apple; b) A set of fully printed chitosan-gated transistors, on flexible edible ethylcellulose substrate, integrated into a pharmaceutical capsule with a medicine.**



# MULTIMODAL NONLINEAR OPTICAL MICROSCOPY FOR BIOLOGICAL APPLICATIONS

Benedetta Talone – Supervisor: Dario Polli

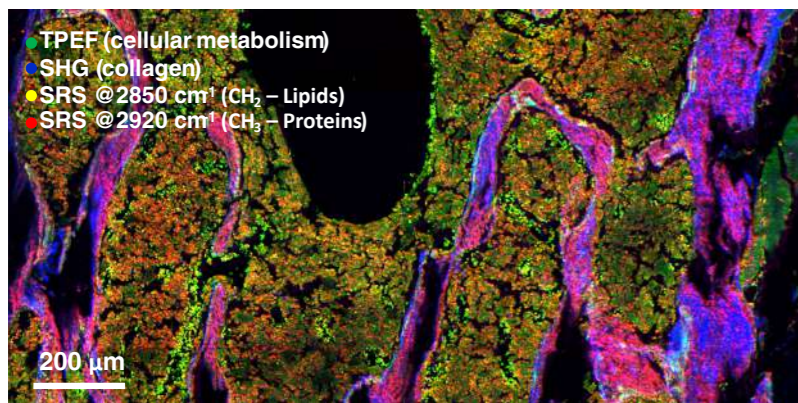
Since its invention, the microscope has been the tool scientists have used to explore the wonders of nature and biology, making visible details otherwise inaccessible to the human eye. Thanks to advances in optics and photonics, microscopes have become increasingly sophisticated and complex instruments, and the introduction of laser illumination has profoundly changed the concept of microscopy, from simple morphological observation to the recognition of chemical structures. When it comes to nonlinear optical microscopy, its extraordinary potential as a rapid, label-free, highly specific, and high-resolution technology has been shown, as have its advantages over traditional techniques. In addition, there is also the possibility of combining several nonlinear microscopy modalities in a single microscope, to fully exploit the information capacity that multimodal images can provide. As a result, a single view is enhanced with multiple complementary contrast processes, allowing for

the simultaneous acquisition of morphological and chemical-functional information from a single observation. In this scenario and considering the increased use of pulsed lasers in biophotonics applications, ensuring that the object is not damaged by the laser during observation is of paramount importance. Unfortunately, the laws governing the occurrence of photodamage in the interaction between light and biological material still conceal mysteries, and the empirical approach is the preferred one to address this problem. I began my Ph.D. studying the reaction of tumor cells to near-infrared ultrashort pulsed laser light exposure. We characterized the survival rate of HeLa cells, an immortalized cervical cancer cell line, irradiated with 130-fs pulses at 1040 nm wavelength and 80 MHz repetition rate, in two different illumination configurations as a function of laser power, scanning speed, and exposure time. Experimental results were analyzed using a data-driven approach

and then verified with thermodynamic considerations, in order to provide useful insights into safe working conditions to many researchers planning experiments involving laser illumination. In VIBRA – Nonlinear Optical Microscopy Lab, we developed an innovative multimodal label-free nonlinear optical microscope, utilizing off-the-shelf components. As well as the possibility of acquiring bright-field images, this microscope can work in four nonlinear different modalities: two multiphoton microscopy techniques, which are two-photon excitation fluorescence (TPEF) and second harmonic generation (SHG), and two vibrational microscopy techniques, coherent anti-Stokes Raman scattering (CARS) and stimulated Raman scattering (SRS). Working in partnership with Humanitas –Clinical and Research Centre, we decided to apply our technology to image murine spine section samples. The project's goal was to investigate the involvement of the enzyme dipeptidyl peptidase 3 (DPP3) in bone pathology as well as the maintenance of bone homeostasis. Bone tissue is a specialized connective tissue with organic and inorganic components. The organic component is mostly made of elastic type I collagen fibrils, organized in a honeycomb matrix to enhance fracture resistance. The inorganic component consists mainly of hydroxyapatite crystals, a mineral salt whose bonds make the collagen matrix rigid and hard. Thus, we compared images, obtained with our multimodal microscope, of samples from healthy mouse models (WT) with samples in which DPP3 deficiency

was induced (KO). With bright-field images, we obtained morphological information on the vertebrae sections under observation. By exploiting the non-centrosymmetric structure of collagen fibers, we studied collagen production and fibrils orientation with the SHG imaging modality. By collecting the autofluorescence signal in the TPEF imaging modality, we mapped the distribution of metabolically active areas through the excitation of intrinsic intracellular fluorophores, such as NADH and FAD. Tuning the SRS imaging modality on wavenumbers resonant with CH<sub>2</sub> and CH<sub>3</sub> bonds, 2850 cm<sup>-1</sup> and 2920 cm<sup>-1</sup> respectively, we measured the concentration of lipids and proteins. In Figure 1 the detail of a multimodal image of KO murine vertebra section. Thanks to our multimodal microscope, we were able to highlight differences between the two mouse models that had not been revealed with traditional techniques, quantifying related biological changes. NLO microscopy techniques have proven to be valid and effective in the study of bone pathologies and a precious tool for biological research, thanks to their label-free, chemically selective, and non-invasive properties. As already said, optical microscopes are essential tools in many scientific fields. Although they are built with excellent optical components, their performance depends on the optical characteristics of the sample under observation. In fact, variations in the refractive index of the sample cause the introduction of optical aberrations that compromise the quality of the image produced. An answer to this problem has been provided by adaptive optics, being able to compensate for aberrations and allow

microscopes to operate at their full potential. Aberrations can be modeled as a linear combination of elements of an orthogonal base. It is well known that the quality of aberration correction depends on the chosen base. A key feature of the base, which ensures that the center of mass of the point spread function of our system remains unchanged during correction, is that it is gradient orthogonal. While it has been shown that the Lukosz Polynomials base possesses this characteristic for linear processes, no known basis has been shown to be so for multiphotonic processes. This means that applying sensorless adaptive optics to nonlinear microscopes introduces shifts in the point spread function during aberration correction, altering the imaging result. We successfully overcome this issue by proposing an experimental method to determine shift-less aberration bases for nonlinear microscopy applications. The base generated by our method was tested on in vivo measurements of the mouse brain and produced better results in terms of resolution and intensity after correction than the usually employed Zernike Polynomials base.



**Fig. 1**  
Multimodal image of KO murine vertebra section.

## STUDY OF THE INTERFEROMETRIC AND GRAVITATIONAL BEHAVIOR OF ANTIMATTER

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The QUPLAS experiment (QUantum interferometry and gravity with Positronium and LASers) aims to study the interferometric and gravitational properties of antimatter. The experiment has been conceived in three phases of increasing sophistication: Positron interferometry (QUPLAS-0), Positronium (Ps) interferometry (QUPLAS-1) and Gravitational acceleration of a Ps beam (QUPLAS-2). The first phase QUPLAS-0 was successfully completed just before the beginning of my PhD and involved the realization of the first antimatter interferometry measurement. The attention of the experiment in the second phase QUPLAS-1 is directed towards interferometric studies of the positronium atom. This measurement would be the first interferometry measurement with a system that is not entirely composed of either matter or antimatter. The interferometric studies of antimatter are interesting also because they constitute a verification of the CPT symmetry between matter and antimatter. Finally the more ambitious and long-term goal of QUPLAS-2 is to study the gravitational behavior of antimatter. This type of study is performed to verify for the first time the weak equivalence principle (WEP), or universality of free fall (UFF) between matter and antimatter. This principle states that if an object is placed at a given point in the spacetime with a given initial velocity, its trajectory is independent of its composition and internal structure. If this principle is true, matter and antimatter should be affected by

the same acceleration within the gravitational field. If instead there were a violation for antimatter, then the value of the gravitational acceleration could change both in sign and in module, with enormous repercussions on fundamental physics and cosmology. QUPLAS-2 aims to perform this measurement using a positronium beam. During the first two years of my PhD studies I was directly involved in the characterization of two different antimatter detectors which will be fundamental in the next phases of QUPLAS. The first detector is the nuclear emulsion and it has been characterized in terms of detection efficiency to low-energy positrons (below 20 keV). This characterization demonstrates the feasibility of using this detector in a low energy regime and defines the limits of use for gravitational studies with antimatter. During the second year of my PhD studies I was involved in the characterization of a second type of detector in the same energy range: the Microchannel Plate Detector (MCP). Even if its spatial resolution is lower with respect to nuclear emulsions, the MCP offers some advantages, for example the possibility to monitor a particle beam in real time. During the last year of my PhD I have been involved in the design of the positronium beam needed for positronium interferometry (QUPLAS-1). Positron interferometry, observed for the first time in QUPLAS-0 was a very successful result. Now positronium involves new difficulties and challenges. The Ps atom is an unstable system

that undergoes annihilation with a very short lifetime (140 ns for the spin triplet state and 0.125 ns for the singlet state). In addition to this the overall electric charge is zero and therefore it cannot be accelerated and guided with uniform electric fields to form a beam with characteristics suitable for interferometry. Recently an innovative method has been proposed for the realization of a positronium beam. This involves the use of the Ps negative ion: the Ps<sup>-</sup> (e<sup>-</sup> - e<sup>+</sup> - e<sup>-</sup>). This ion can be easily controlled with electromagnetic fields and after the beam formation, it is possible to remove one of the electrons through laser photodetachment to obtain a neutral positronium beam. Positrons are generated by the  $\beta^+$  decays of a <sup>22</sup>Na source and implanted in a mono-crystalline tungsten foil (W[100], 1  $\mu$ m thickness). This tungsten sample has a negative work function for Ps<sup>-</sup> and therefore a fraction of the implanted positron binds to two electrons and is spontaneously reemitted from the surface in a transmission geometry. The Ps<sup>-</sup> emission surface will be decorated with sodium (a monolayer or less), since it has been observed that the emission is favored when an alkali metal is deposited. The Ps<sup>-</sup> formation strongly depends on the surface dipole barrier D and in particular it would be useful to reduce the value of D as much as possible. The deposition of an alkali metal on the surface of the converter produces exactly this effect. Once the ions are emitted from the converter they must be electrostatically accelerated and guided in a beam of

low angular divergence. During my PhD studies I was directly involved in the design of an electrode system for this purpose through simulations with the SIMION software. This program allows one to define the geometry of the electrodes and it computes the trajectories of the particles within the electric fields. The developed system is designed in order to accelerate the Ps<sup>-</sup> ions to an energy of 2.625 keV (compatible with the presently available interferometer), focus the beam with a divergence of less than 10 mrad and bend the beam to remove a direct line of sight between the radioactive source and the interferometer (to reduce the background). Once the Ps<sup>-</sup> beam has been properly formed, it is necessary to remove one of its two electrons in order to form a neutral positronium beam. This is done via laser photodetachment. To cope with the extreme laser power required to operate with a continuous beam a high finesse optical cavity in a Fabry-Perot configuration has been developed. In this cavity the laser beam is reflected a high number of times (finesse = 40000) by specially designed mirrors until a power of  $\sim 200$  kW is reached. The cavity will be pumped by a commercial seed laser with a continuous wave (CW) Erbium Fiber Amplifier, which guarantees an input power of 30 W with a wavelength of 1560 nm ( $\sim 0.8$  eV). The photodetachment cross section for this wavelength is  $\sim 6.5 \times 10^{-17}$  cm<sup>2</sup>. Following photodetachment, the positronium atoms continue their trajectory unaffected by electric fields. For this reason, precise guidance of the

Ps<sup>-</sup> beam is required prior to the laser. The Ps<sup>-</sup> ions that have not undergone photodetachment, together with the positronium atoms formed in a singlet state annihilate in a few mm due to their short lifetime. The positronium atoms formed in a triplet state, on the other hand, are able to propagate through the entire interferometer up to the detector. The interferometer, designed in an asymmetric Talbot-Lau configuration, is the same used in QUPLAS-0 for positron interferometry. It consists of two SiN diffraction gratings placed at a distance  $L_1 = 118.1 \pm 0.2$  mm. The periodicity of the two gratings is respectively  $d_1 = 1.2 \mu$ m and  $d_2 = 1 \mu$ m. This produces a magnification effect of the interferometric pattern  $\eta = 5$  at a distance  $L_2 = 576 \pm 5$  mm. Nuclear emulsions will be used to resolve the interferometric pattern with a periodicity of 6  $\mu$ m, thanks to their high spatial resolution. After exposition, the emulsions will be developed through chemical processes and scanned with an optical microscope. The search for the interferometric pattern will be carried out using a Rayleigh test algorithm.