



Chair:
Prof. Paola Taroni

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) Main courses specifically designed for the PhD program; 3) Activities pertaining to more specific disciplines which will lay the foundation for the research work to be carried out during the Doctoral Thesis; 4) 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), INFN-CNR, IIT-Istituto Italiano di Tecnologia.

At present, the number of students in the three-year course is fifty-six, and fifty-five of them have a fellowship.

The PhD Program Faculty, who takes care of organizing and supervising teaching and research activities, consists of a number of members large enough to cover a wide spectrum of research fields. All members (listed here below) are highly qualified and active researchers. 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.

FAMILY NAME	FIRST NAME	POSITION*
BERTACCO	RICCARDO	AP
BRAMBILLA	ALBERTO	AP
CICCACCI	FRANCO	FP
CUBEDDU	RINALDO	FP
DALLERA	CLAUDIA	AP
D'ANDREA	COSIMO	AP
DELLA VALLE	GIUSEPPE	AP
DE SILVESTRI	SANDRO	FP
DUÒ	LAMBERTO	FP
FINAZZI	MARCO	FP
GHIRINGHELLI	GIACOMO	FP
ISELLA	GIOVANNI	AP
LANZANI	GUGLIELMO	FP
LAPORTA	PAOLO	FP
MARANGONI	MARCO	AP
NISOLI	MAURO	FP
RAMPONI	ROBERTA	FP
STAGIRA	SALVATORE	AP
TARONI	PAOLA	FP
TORRICELLI	ALESSANDRO	FP

*Position: FP = Full Professor; AP = Associate Professor.

FAMILY NAME	FIRST NAME	INSTITUTION
PIROVANO	AGOSTINO	Micron Semiconductor Italia s.r.l.
DONATI	FABIO	EPFL – Lausanne, CH
HECHT	BERT	Università di Würzburg, D
LURIDIANA	SEBASTIANO	Tecno Vacuum s.r.l.
BLANDINO	DAVIDE	Optec s.p.a.
MAJORANA	SALVATORE	IIT - Technology Transfer Office

GRAPHENE NANOELECTRONICS: FROM GRAPHENE FIELD-EFFECT TRANSISTORS TO INTEGRATION WITH SEMICONDUCTOR TECHNOLOGY

Luca Anzi - Supervisor: Prof. Roman Sordan

Graphene, the thinnest material known to us, was isolated by the Nobel Prize winners A. Geim and K. Novoselov thirteen years ago. From that point, a “gold rush” took place in the investigation of graphene properties. Its very high conductivity, and flexibility make graphene the perfect material for next-generation flexible electronics.

In conventional electronics, Si and III-V semiconductors are widely used. Si is mainly used in digital electronics because it offers the advantage of a very high scale of integration. The high carrier mobility in III-V semiconductors makes them suitable for high-frequency operations. On the other hand, graphene has the highest carrier mobility ever measured at room temperature, which is more than 10 times that of conventional III-V semiconductors. Although this makes graphene the perfect candidate for high-frequency devices, graphene field-effect transistors (GFETs) suffer from large series resistances and poor drain current saturation, which strongly limits their maximum frequency of operation. My Ph.D. work focused on the optimization of GFET parameters for achieving better DC and AC performances. The main source of parasitic series resistances

is the contact resistance (R_c). R_c is the intrinsic property of the metal-graphene interface and it is independent of the scaling of the transistor channel length. In short-channel GFETs, the contact resistance dominates the overall channel resistance deteriorating the transistor performances. We performed R_c measurements for different type of metals (Figure 1), finding that pure Au provides the lowest contact resistance. To further decrease the contact resistance in our devices, we etched a matrix of holes in the graphene underneath the contacts (Figure 1b and 1c). This increased the edge contact effect and lowered the contact resistance. With this configuration, we could reach $R_c = 23 \Omega\mu\text{m}$, which is the lowest ever reported R_c for graphene-metal contacts. Moreover, this value is also smaller than state-of-the-art R_c in conventional semiconductor technology ($50 \Omega\mu\text{m}$). We also investigated the behavior of contact resistance as a function of the back-gate voltage overdrive (Figure 2). The standard contacts, where surface injection dominates, exhibit maximum R_c at the Dirac point (zero at the voltage axis). Moving away from zero, the density of the states of graphene increases, the injection increases, and therefore the

contact resistance decreases. The behavior of the holey contacts is opposite. Next to the Dirac point, the edge injection dominates, and the contact resistance reaches its minimum. Moving away from zero, the edge injection mechanism is disturbed by the surface injection. The competition between these two mechanisms lead to an increase in contact resistance. Far away from the Dirac point, surface injection dominates again and the contact resistance behaves as in case of the standard contacts. High-frequency transistors should also exhibit a good drain current saturation. The output conductance g_{dr} calculated as the derivative of the drain current with respect to the drain-source voltage (V_{DS}), is the parameter which quantifies the saturation of a transistor. The lower it is, the flatter the output curve is and the better the saturation is. In conventional transistors, the channel next to the drain gets fully depleted (pinch-off) when V_{DS} becomes large enough. A further increase in V_{DS} leads to an enlargement of the depletion region which leads to the drain current saturation. Due to the ambipolarity of graphene, electrons in GFETs starts to be replaced by holes. This raises the conductivity of the channel and increases the drain current

resulting in a so-called quasi-saturation region. To modify this behavior and reduce g_{dr} , we replaced the Au drain contact with a Ni-Al contact (Figure 3a). The electrostatic doping of graphene next to the drain was changed from p-type to n-type due to the Ni-Al contact. Such asymmetric contact configuration led to a non-uniform doping of the GFET channel. This reduced the accumulation of holes at V_{DS} above the pinch-off point. The final effect is a more pronounced saturation region as shown in Figure 3b. In our experiments, we were able to reduce g_{dr} by at least 3 times with respect to that of the standard Au contacts.

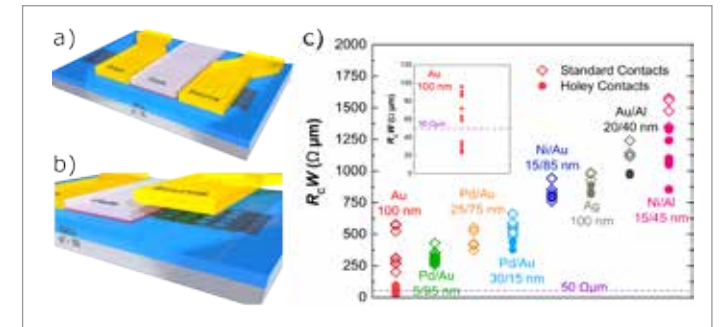


Fig. 1 - a) Schematic of a GFET with holey contact; b) Holes are etched in the graphene underneath the contacts; c) Contact resistances for standard and holey contacts made of different metals. The inset shows contact resistance for holey Au contacts.

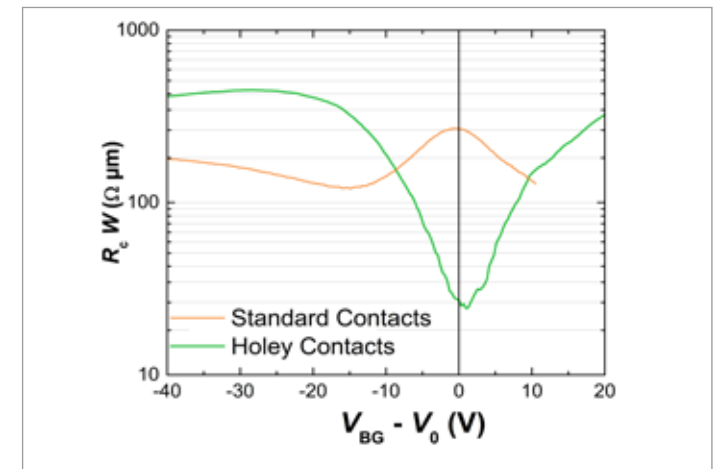


Fig. 2 - Contact resistance versus back-gate voltage overdrive for standard contacts (orange) and holey contacts (green)

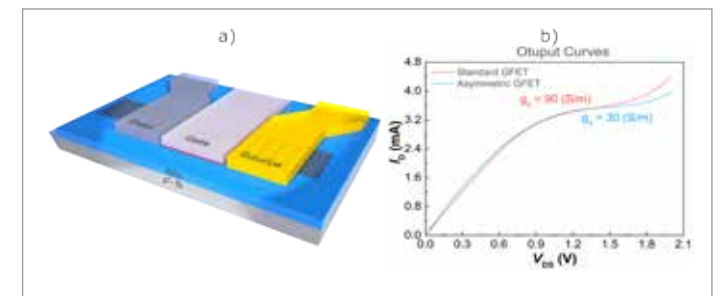


Fig. 3 - a) Schematic of a GFET with asymmetric contacts. The source is made of Au whereas the drain is made of NiAl; b) Comparison of output curves of asymmetric GFET and standard GFET. The current saturation is better, i.e., the g_d is smaller in the GFET with asymmetric contacts.

GERMANIUM AND SiGe EPITAXIAL GROWTH FOR MID-INFRARED APPLICATIONS

Andrea Ballabio - Supervisor: Prof. Giovanni Isella

The development of silicon photonic has a strong impact on several applications, such as integrated communications, optical interconnects, computing and manipulation of light at the chip scale. Nowadays, silicon photonic devices operate in the near-infrared range selecting the well-known 1.55 μm and 1.30 μm , as preferred wavelengths. The standard silicon photonic platform is based on silicon-on-insulator (SOI) substrates, in which the silicon is used as waveguide, while the SiO_2 works as a cladding layer. Recently, the possibility to extend the wavelength range to the mid-IR, given by the development of the quantum cascade laser that provides a tunable and coherent light source in the mid-IR, attracted the interest of the researchers, due to the different applications achievable in this wavelengths region besides the standard data communications, such as on-chip chemical and biological sensing and integrated non-linear optics. However, the Si/ SiO_2 platform cannot be used in the mid-IR due to the high absorption of the SiO_2 above 3 μm . For this reason, the development of an alternative platform is necessary. The main goal in this field is the realization of active and passive components operating in the mid-IR, employable as a building

blocks for a mid-IR photonic platform. The first issue to overcome is the choice of the materials to be used in this wavelength range. Different groups come up with valid approaches to find a suitable platform, which involve SiN as cladding layer, suspended Si waveguide and chalcogenide waveguides. Ge waveguides have also been considered due to the wide transparency and the easy integration of Ge on Si. Thus, Ge, SiGe alloys and Ge/SiGe heterostructures are good candidates for realizing the basic building blocks for mid-IR photonics, which are expected to offer high performances, due to the material's properties, and low cost and low fabrication issues, due to the high compatibility with standard silicon technologies.

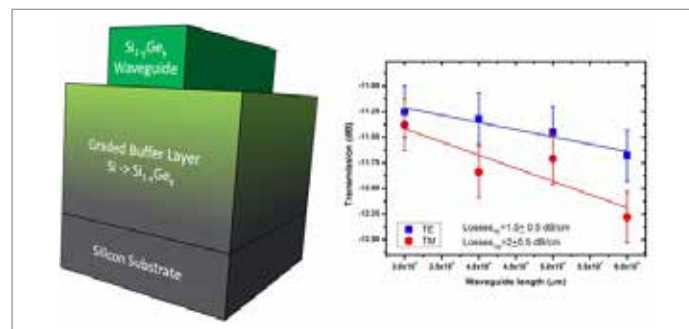


Fig. 1 - On the left: schematic of the structure of the waveguide. On the right: transmission measurement as a function of the waveguide length for TE and TM mode. The extracted losses for the waveguide are reported.

Additionally, just like silicon photonic, germanium-based photonic can be monolithically integrated on CMOS devices, in order to fabricate optoelectronic integrated circuits. This could be relevant for the realization of fully functional lab-on-chips. During my PhD, I exploited the properties of the Ge and SiGe alloys, to realize devices and structures working in the mid-IR. Taking advantage of the transparency of the Ge, and the tunable refractive index of the SiGe alloy, I will present the realization of Ge-based mid-IR waveguides showing good performances in term of losses, which have been used to fabricate passive components as Mach-Zender interferometer.

Furthermore, manipulating

the properties of SiGe heterostructures it is possible to realize light absorber working in the mid-IR, exploiting the intersubband absorption in Ge/SiGe quantum wells. I will show the approach we used in order to produce p-type Ge/SiGe quantum wells able to absorb light at a desired wavelength in the mid-IR.

Non-linear optic effects are also a relevant topic in term of applications, since they give the chance to create light source, as supercontinuum laser, or enhancing the sensing capabilities of a device. Si and Ge have a zero χ_2 due to their centrosymmetric structure, but they can be used as third order non-linear materials, having a non-zero χ_3 and, additionally, the presence of heterostructures could enhance the non-linear properties of the material.

In this context, parabolic quantum wells (PQWs) are interesting structures, because the presence of equally spaced levels within the quantum well is relevant to enhance non-linear effects. In this work, I have realized Ge parabolic quantum wells by means of Low-Energy Plasma-Enhanced Chemical Vapor Deposition. I have analysed the material with structural (XRD) and optical measurements (transmission

and photoreflectance), to test the properties of the parabolic profile.

Moreover, the PQWs system offer the chance to test a fundamental property of the Ge/Si heterointerface which is still discussed in literature, that is the band offset at the heterointerface of the two materials. I extracted

the value of the natural valence band offset between Si and Ge, by comparing photoreflectance measurements and $k \cdot p$ simulations carried out on the PQW structure.

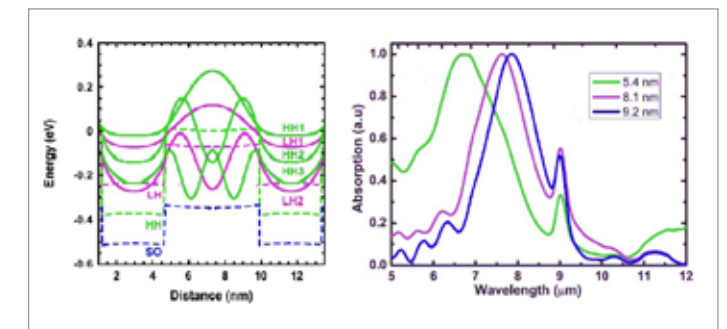


Fig. 2 - On the left: a schematic diagram of the calculated valence band of the quantum well structure, with the subband state for the HH and LH. On the right: mid-IR absorption measurements of three QWs structure at room temperature.

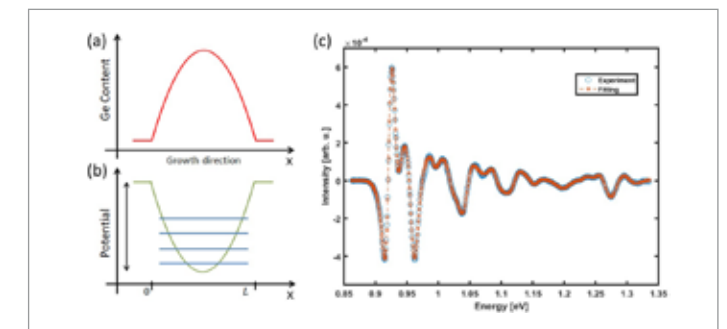


Fig. 3 - (a) Schematic of the Ge profile of a PQW. (b) Representation of the band of the PQW, equally spaced energy levels defined by the harmonic oscillator solutions are shown. (c) Example of a photoreflectance spectrum of a PQW, the experimental data and the first derivative line shape fitting is shown.

FEMTOSECOND LASER MICROFABRICATION OF 3D PHOTONICS CIRCUITS IN DIAMOND FOR QUANTUM INFORMATION AND MAGNETOMETRY

Vibhav Bharadwaj Shivakumar - Supervisor: Shane Eaton

Tutor: Roberta Ramponi

Diamond's nitrogen-vacancy (NV) center has been shown as a promising candidate for sensing applications and quantum computing because of its long electron spin coherence time and its ability to be found, manipulated and read out optically. An integrated photonics platform in diamond would be useful for NV-based magnetometry and quantum computing, in which NV centers are optically linked for long-range quantum entanglement due to the integration and stability provided by monolithic optical waveguides. Femtosecond laser writing has been shown as a powerful fabrication tool that has already shown its capability to produce integrated photonic circuits in glasses. Extending the use of this technique to diamond could enable photonic circuits along with the single-photon sources (NVs) on the same chip. In addition, femtosecond laser processing could be applied to form both photonic and microfluidic components together with the NVs to produce compact sensing devices. We have used laser writing for laser inscription of the first waveguide in the bulk of diamond using type II modality of laser writing, with a mode field diameter of about 10 μm and an insertion

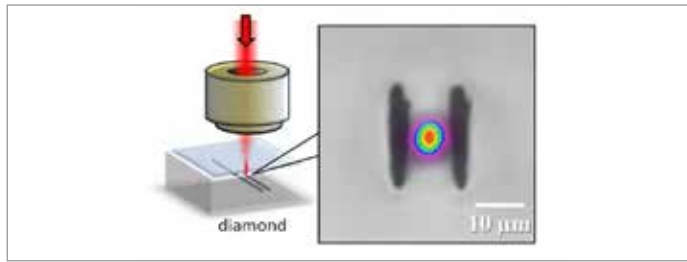


Fig. 1 - Schematic showing laser writing of Type II waveguide in diamond and the transverse optical microscope image of type II waveguide with the mode at 635 nm wavelength.

loss of about 11 dB for the 5 mm long waveguide at 635 nm wavelength, as shown in Figure 1. By laser writing additional two lines vertically separated, single mode guiding at visible wavelengths was achieved. By employing free space coupling of high power 532 nm wavelength laser into the waveguide and collecting the optical spectrum at the output, it was seen that the waveguides preserve the NV photoluminescence (PL). Motivated by the wide transparency of diamond from 220 nm up to terahertz regime, waveguides with large separation were laser written for guiding at 2.3 μm and 8.7 μm wavelengths. Additionally, Bragg grating waveguides for wavelength selective reflection were laser written by creating periodic modification of periodicity 1.3 μm over the two modifications

of the type II waveguide and hence creating a refractive index modulation along the waveguide. The resulting transmission spectrum showed a narrow dip at 1552 nm of about 6.5 dB, impressively high for a 4th order grating. Bragg grating waveguides are beneficial for fabricating cavities in diamond for Raman lasers, for enhancing the NV excitation or to filter the excitation wavelength.

Deterministic placing of NV centers in the bulk is of utmost importance for integrated diamond photonics. Conventional technique of placement using ion implantation requires high energy ions for deep NV implantations which also suffers from straggling effect leading to distortion in the focus. Additionally, high energy implantations create undesirable stress detrimental to the NV

spectral properties. Femtosecond laser writing has shown to create color centers in glasses and other crystals. Employing femtosecond laser writing, single laser pulse exposures with varying pulse energies were laser written in diamond at a depth of 25 μm . Subsequent annealing at 1000°C for 3 hours led to the mobilization of the vacancies and eventual trapping with a nitrogen atom in the vicinity to form the NV centers. Confocal PL measurements performed revealed a spatial resolution of placement of less than 1 μm . Second order intensity autocorrelation performed indicated single photon emission from the laser written NV centers.

Integration of the optical waveguide and deterministically placed NV centers is of paramount significance. In this endeavor, static exposures were laser written within type II waveguides for optical coupling of the waveguide – NV using the same femtosecond laser writing setup. Initial overhead PL map obtained from the waveguide showed a bright emission from the NVs from within the waveguide. The NV center within the waveguide was excited through the waveguide and the emission was collected from overhead microscope objective into EMCCD to obtain the PL map, as shown in Figure 2. Second order intensity correlation performed on the emission showed single photon emission. Additionally, optical excitation of the NVs from overhead microscope objective and collection of the emission along the waveguide was performed showing the position of

the NV to be well coupled with the waveguide mode.

In conclusion, we have shown femtosecond laser writing as a powerful tool for integrated quantum diamond photonics, as shown in Figure 3, offering the ability to laser write waveguides in the bulk of diamond, where the NV spectral properties are enhanced. The optical waveguides provide easy compatibility with existing optical fiber technology excitation

and collection of the NV signal. We have also shown the ability to deterministically place NV centers in the bulk of diamond using single laser pulse. The integration and optical coupling of the laser written waveguide and NVs is very beneficial for the creating more complex devices for quantum sensing and magnetometry.

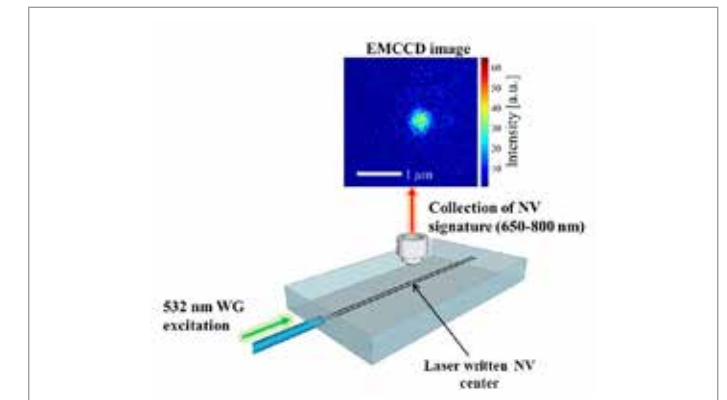


Fig. 2 - Schematic showing the EMCCD image obtained by exciting the laser written NV through optical coupling of the laser written waveguide with optical fiber.

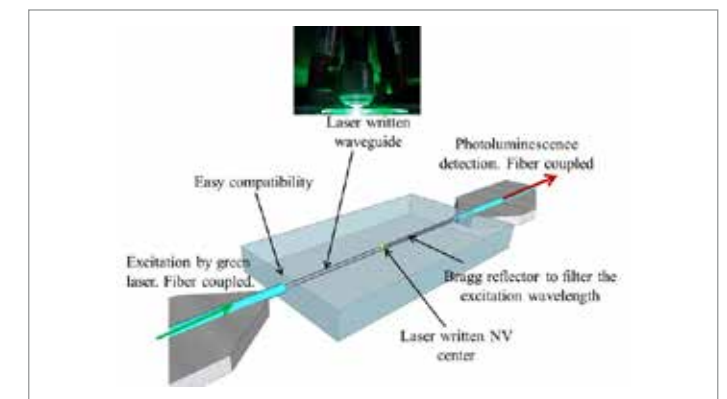


Fig. 3 - Schematic showing an integrated Quantum device fabricated by laser inscription of photonic components in diamond.

EDIBLE AND CARBON-BASED FUNCTIONAL MATERIALS FOR NOVEL ORGANIC BIOELECTRONIC DEVICES

Giorgio E. Bonacchini - Supervisor: Dr. Mario Caironi

In recent years, organic bioelectronics has emerged as potentially disruptive technology, introducing innovative devices with unprecedented features of biocompatibility and functionality. The potential of this class of materials resides not only in their favourable mechanical properties, which comply to those of biological tissues, but also on their ability to enable mixed electronic and ionic transport and on the possibility to finely tune their optoelectronic properties, such as optical absorption, charge photogeneration and transport. In addition, the synthesis of organic small molecules and polymers can be tuned to further improve biocompatibility and to allow for chemical or biochemical functionalization (bioconjugation), as well as to enable cost-effective and scalable processability of materials. For these reasons, a plethora of mechanically compliant, large area, multipoint biosensing and stimulating devices are now available, able to operate on irregular surfaces and in contact with biological tissues and environments. Existing technologies range from either chronic or transient implantable biosensors and drug-delivery systems, to electronic transducers for *in vitro* and *in vivo* neuronal activity, artificial retinas,

electrochemical ion pumps and ingestible devices. Moreover, research on disposable lab-on-a-chip systems and epidermal electronics has also fostered attention towards solutions supporting novel interaction routes between biological systems, bioelectronics devices, and commercial consumer electronics, such as smartphones and other portable devices. Among the several applications of organic bioelectronics, increasing interest is currently being dedicated to the development of electronic devices and systems that can be safely ingested, to perform relevant therapeutics and diagnostics from within the gastrointestinal tract. Edible electronics could have a significant impact on clinical environments, nevertheless it holds an even greater potential in the development and diffusion of novel point-of-care systems. The concept driving point-of-care technology is to conveniently bring biomedical tests and therapeutics in proximity to the patient, improving the rapidity, the effectiveness and the efficiency of medical analyses and treatments, as well as decrease overall healthcare costs. Moreover, this technology could enable innovative *smart labelling* strategies to address food

and pharmaceuticals tracking, identification and monitoring along the product distribution chain. By incorporating edible electronic biosensing systems directly onto foods, it would indeed be possible to exploit the intimate contact between devices and aliments to monitor food parameters, pathogen proliferation and environmental conditions during preparation, delivery and stocking. For these reasons, in recent years, stronger efforts have been dedicated to the realization of edible devices with biocompatible organic materials, capitalizing on the remarkable progresses made in the contexts of organic and flexible electronics. As a matter of fact, the favourable mechanical and chemical properties of organic compounds largely reduce the possibility to incur in gastrointestinal obstruction or device retention in the organism, thanks to the *soft* nature of these materials, and to the possibility to allow for their controlled degradation in the aqueous biological environment. Finally, a further advantage in using organic compounds lies in the ease of processability by cost-effective and up-scalable solution-based techniques, such as inkjet printing, which are fundamental to guarantee large-scale diffusion of this technology

in both biomedical and food monitoring applications, also in Third World countries. A number of edible organic devices have thus been proposed, including edible batteries, supercapacitors, THz resonators arrays for food quality monitoring, piezoelectric gastrointestinal motility sensors and biocompatible organic field effect transistors fabricated on edible substrates. In this dissertation, temporary tattoo-paper is proposed as a simple and versatile platform for the integration of electronics onto food and pharmaceutical capsules. Specifically, it is demonstrated the fabrication of all-printed Organic Field-Effect Transistors (OFETs) and elementary circuits, realized with edible or biocompatible materials, on untreated commercial tattoo-paper, and their subsequent transfer and operation on edible substrates with a complex non-planar geometry. Different types of small-molecule and polymer semiconductors were used to demonstrate the versatility of the transfer procedure and the compatibility with both good hole and electron transporting materials, as required by robust complementary logic circuits. Specifically, we investigated the transport properties of edible materials, such as food dyes and pigment, as well as well-known

biocompatible semiconducting polymers. High-performance donor-acceptor copolymers with reported field-effect hole and electron mobilities that exceed $1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, have been also exploited for both p-type and n-type devices. While testing the tattoo-transfer methodology with high-performance donor-acceptor co-polymers is a relevant choice to express the full potential of the edible technology, no account on biocompatibility of these materials is currently available. For this reason, a set of cell-proliferation assays has been performed for the first time on these materials, using human cell lines from both the upper and lower intestine, to determine their potential biocompatibility, showing no sign of cytotoxicity. The tattoo-paper approach thus constitutes a simple and versatile mean for the integration of fully printed organic circuitry onto food and pharmaceutical drugs, and the proposed transfer procedure is robust, being validated on a statistically relevant number of devices, and does not alter the integrity of ingestible substrates. In conclusion, the use of commercial tattoo-paper for the integration of biocompatible active electronic devices on edible substrates opens new and exciting possibilities in the long-term

vision of widely accessible personal care applications: it is compatible with cost-effective and mass-manufacturing printing techniques, and it provides a general and flexible platform for easy integration of the devices on many different types of objects, without any type of surface treatment prior to device fabrication or transfer.



Fig. 1 - Photograph of an array of organic transistors transferred on a commercial pharmaceutical capsule by means of tattoo-paper transfer.

ULTRAFAST TIME-RESOLVED PHOTOEMISSION SPECTROSCOPY OF NOVEL COMPLEX MATERIALS: FUNDAMENTAL PHYSICS AND APPLICATION PERSPECTIVES

Davide Bugini - Supervisor: Ettore Carpene

Tutor: Claudia Dallera

In the past few decades, the emergence of mode-locked ultrashort pulsed lasers has triggered the development of new techniques to study the ultrafast electronic dynamics. This novel approach offers the opportunity to unfold unsolved problems in solid state physics and in other branches of science. In addition, the emergence of novel quantum materials (e.g. high-Tc superconductors, topological materials) and the increased interest on their properties in view of faster generation of (opto-) electronic devices required a deeper attention to the out-of-equilibrium phenomena. In this framework, time and angle resolved photoemission spectroscopy (TR-ARPES) deserves a special mention since it is the only technique offering the capability to access the electronic dynamics directly in the reciprocal space, i.e. the electronic band structure. In TR-ARPES an ultrashort infrared/visible pump beam brings the electronic system out of equilibrium while an ultraviolet probe beam tracks the relaxation dynamics on a temporal scale ranging from a few tens of femtoseconds to picoseconds. During my Ph. D., I investigated two classes of materials with TR-ARPES:

Topological Insulators (TIs); Low-dimensional materials exhibiting metal-to-insulator phase transition. The TR-ARPES measurements have been done on the cutting-edge Yb-laser based setup developed at the Ultrafast Photoemission and Optical Spectroscopy (UPhOS) laboratory in the Physics department of Politecnico di Milano. Thanks to a cascade of non-linear optics processes (e.g. Non-collinear Optical Parametric Amplifier (NOPA) and Sum Frequency Generation (SFG)), a sub 30-fs 1.8 eV pump beam and a sub 70-fs 6-eV probe beam have been achieved. The temporal resolution is around 70-fs. Photoemitted electrons are collected by a home-made time of flight (ToF) analyzer with an angular acceptance of 0.8° and an energy resolution around 50 meV. Topological Insulators are a recently predicted and discovered phase of matter characterized by an in-plane spin-polarized surface states (TSSs) arising within the bulk insulating energy gap. The protection against spin-flip events and the capability to control the spin polarization using ultrashort light pulses open new scenarios in the use of this class of materials for future opto-spintronic devices. Thus, TIs have

become a hot-topic in the scientific community since they promise a new generation of faster devices. Using TR-ARPES on the $\text{Sb}_x\text{Bi}_{(2-x)}\text{Se}_y\text{Te}_{(3-y)}$ class we studied the response of spin-polarized electrons to ultrashort circularly-polarized pulses. We reported the first experimental evidence of a direct coupling between circular light and the empty topological surface state (ESS) located within a bulk-gap of the unoccupied states. We observed also the establishment of a flow of spin-polarized electrons along the ESS branch i.e. an ultrafast photon-induced spin-current. In addition, our data suggest an accumulation of spin-polarized electrons in the conduction band of TIs due to the spin-dependent decay channels. These observations are promising milestones for the development of a generation of TI-based opto-spintronic devices. In the last decade, the discovery of graphene boosted research in the field of low-dimensional materials. In fact, peculiar properties such as the very-high carrier mobility are crucial for a revolution in the electronics. Despite these promising properties, the lack of a band-gap, fundamental for any operative electronics device, is a limiting factor in the implementation of graphene.

Thus, low-dimensional condensed matter systems that exhibit a metal-to-insulator transition attracted a lot of attentions in the material science community. This class of materials provides in fact the unique possibility to drive and control the opening and closing of the band gap by an external parameter like temperature, fundamental requirement for a less-consuming and computationally faster electronics. The opening of the gap below a critical temperature is due to the formation of a modulating low energy excitation called charge density wave (CDW) that is closely related to a periodic lattice distortion. Although this transition is well-known since the '60s, the underlying mechanism is not well-established and understood. In addition, it has been observed that CDWs are in competition with the formation of the high-temperature superconductive phase. Thus, a better understanding of the forces driving the transition could help get the knots of the still mysterious high-Tc superconductivity. We investigated the photo-induced melting of CDW in 1T-TiSe_2 single crystals by TR-ARPES. Our measurements reveal that after photo-excitation different dynamics arise in the closing of the band-gap and in the melting

of the charge order suggesting an excitonic-lattice cooperative model. The quasi one-dimensional system $(\text{TaSe}_4)_2\text{I}$ is at the center of a research project performed in my Ph. D. at École Polytechnique Fédérale de Lausanne (EPFL) and supported by the Excellence Swiss Federal Government Scholarship for research. This compound represents a novel and promising point of contact between topological quantum materials and the CDW's metal-to-insulator transition class. Theoretical calculations have in fact predicted a topological Weyl phase while the system transits in the metal phase above the critical temperature. Weyl materials are extremely interesting due to their unprecedented ultrahigh carrier mobility (as in graphene) and for their unique electronic transport properties under an external magnetic field. These properties make Weyl materials the ideal candidates for the realization of quantum computers. The idea of the project is to exploit TR-ARPES to optically induce and characterize a transition from the insulating to the Weyl phase in $(\text{TaSe}_4)_2\text{I}$. In this way this system could work as ultrafast-optically driven logic switcher in the next generation of computational

devices. In conclusion, TR-ARPES is an excellent tool for understanding fundamental properties of novel quantum systems and low-dimensional materials. Exploiting this technique in my Ph. D. research activity we have contributed to unfold the mechanism at the origin of the charge density wave phase in 1T-TiSe_2 , answering a long-standing fundamental question and adding a new piece to the unsolved puzzle of high-Tc superconductivity. Our TR-ARPES measurements on topological insulators disclosed the contribution of the spin-dependent decay channels in the electronic dynamics and suggested the capability to optically drive an ultrafast spin-current in these materials.

ULTRAFAST SPECTROSCOPY OF ZERO AND TWO-DIMENSIONAL MATERIALS FOR PHOTONIC APPLICATIONS

Andrea Camellini - Supervisor: Prof. Margherita Zavelani-Rossi

The request of clean and efficient energy sources with minimal environmental impact is leading the scientific community toward the development of innovative devices capable of exploiting sunlight radiation. In this context, an important issue that has to be addressed by any solar energy conversion device, is related to the light harvesting efficiency. Two main strategies can be pursued: the enlargement of the energy spectral range which can be collected and the increase of the absorption capabilities. The development of new photonic devices employing engineered low dimensional materials with devoted functionalities is a very promising route towards these challenging goals. In this PhD thesis, I studied the evolution of non-equilibrium processes in two classes of nanomaterials properly designed for sunlight harvesting applications. In particular, I analyzed colloidal semiconductor nanocrystals (0-dimensional) and two-dimensional transition metal dichalcogenides.

Colloidal semiconductor nanocrystals (NCs)

Colloidal NCs are nm-size crystallites of inorganic semiconductor characterized by both molecular and bulk-like properties. The term "colloidal" means that these NCs are

synthesized through highly-reproducible chemical procedures able to provide NCs with very low size dispersion. Technological advancements in the synthesis procedure allows to control both size, shape, stoichiometry and provide different types of heterostructures. Heterostructuring provides also an effective strategy to overcome detrimental non-radiative recombination mechanisms acting on an ultrafast time scale (few to tens of picosecond) to be circumvented for the implementation of NCs in real devices. Altogether this allows wavefunction engineering and thus to obtain NCs with optical band gaps spanning from the visible to the near infrared spectral region and controlled optoelectronic properties. In the thesis, we compare three different types of NCs made of PbS and CdS in a core/shell arrangement, with different shell sizes and core/shell interfaces, active in the near infrared spectral region. We study the NCs by means of transient absorption (TA) spectroscopy with sub-picosecond time resolution and steady state photoluminescence (PL). By selective excitation of the PbS core or of the CdS shell, and combining evidences from TA and fluence dependent PL, we demonstrate

that, regardless of shell dimensions and type of interface, PbS/CdS NCs are able to sustain a delocalized electron population throughout the core and shell domains. This explains the peculiar PL behavior characterized by the presence of two simultaneous peaks in the spectrum at different wavelengths originating from core and shell regions, for any kind of PbS/CdS NC. The recombination of photo-excited carrier, instead, strongly depend on shell volume and type of interface. In particular, we demonstrate that a large shell volume favors both a decoupling of core and shell recombination processes and, as a direct consequence, the reduction of the multicarrier non-radiative decay processes. A complementary evidence of this was obtained by the observations, of amplified spontaneous emission (ASE) from the shell domain, in a drop-casted films, under 150fs pulse excitation. Furthermore, by studying the ultrafast charge transfer from the NCs to an organic electron scavenger we demonstrate that the large shell volume does not prevent any charge transfer to occur. Our findings provided noteworthy information for implementation of PbS/CdS nanocrystals with large volume ("giant") shell in real devices. As a result, the

properties of these NCs were verified in photoelectrochemical (PEC) cells. A PEC cell sensitized by "giant" PbS/CdS NCs with an alloyed interface has shown to extend the absorptive spectral range of the photoanodes and to be characterized by a higher photocurrent density and a longer stability compared to PEC cells sensitized with PbS/CdS heterostructures with thinner shell.

Two-dimensional transition metal dichalcogenides (TMDs)

Since the advent of graphene, great effort has been devoted toward the synthesis of two-dimensional materials with semiconducting band-like structure and high values of carrier mobilities for photonics and nanoelectronic applications. TMDs represent one of the most promising option for new devices characterized by high performances. Despite their nm-size thickness, stacked few layers of TMDs present high values of optical absorption in the visible spectral range due to the excitonic nature of their primary excitations which make them feasible, as already demonstrated, for integration as absorbing layer in ultrathin photodetectors. A modification of the optical absorption can be obtained by introducing anisotropic

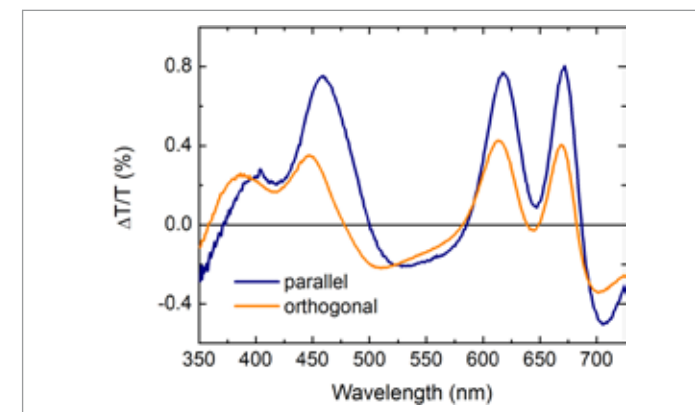


Fig. 1 - Transient transmission spectra of 4 layers MoS₂ deposited onto a nano-corrugated glass substrate endowed with a uniaxial corrugation. Optical anisotropy is evidenced by a different spectral response for the parallel and orthogonal directions with respect to the corrugation axis.

degrees of freedom in the spatial arrangement. In this context, a novel fabrication methodology for glass substrate nanostructuring together with the demonstration of subsequent conformal chemical vapor deposition of TMDs onto them, have enabled the production of artificially designed anisotropic large area (cm² scale) TMDs nanosheets. Here we study by means of linear transmission and TA spectroscopy the modification of linear and non-linear optical properties of a molybdenum disulphide (MoS₂) nanosheet with a uniaxial corrugation induced by a nanostructured substrate. Besides an increased light trapping efficiency, we found that the

opto-electronic properties of MoS₂ are dramatically affected by the anisotropic morphology. In particular, MoS₂ acquires a polarization sensitive behavior which is clearly revealed both in static and transient domain (Figure 1) and can be tentatively ascribed to a prominent role of the out-of-plane component of MoS₂ dielectric permittivity enhanced by the corrugated substrate. Our results highlight the possibility to manipulate, by substrate pattern design, the optoelectronic properties of TMDs giving important hints for applications in photonic devices.

DEVELOPMENT OF ULTRAFAST SOURCES FOR APPLICATIONS IN SPECTROSCOPY AND STRONG-FIELD PHYSICS

Anna Gabriella Ciriolo - Supervisor: Caterina Vozzi

Over the last few decades, the development of ultrafast laser sources led to remarkable advances in the field of spectroscopy, providing a powerful technology for studying atomic, molecular and solid state dynamics on an ultrashort time scale, down to the attosecond domain. The increasing interest in exploring the ultrafast matter response under a variety of energy and frequency regimes is driving laser science towards novel approaches allowing for energy and frequency scalability. Moreover, the appealing perspective of making the ultrafast technology accessible for applications outside a few cutting-edge laser laboratories, is boosting the research towards the development of compact and easy-to-handle optical setups. My Ph.D. work concerns the development of ultrafast sources for strong-field applications, including High-order Harmonics Generation (HHG) and Attosecond Pulse Generation (APG). Here, I provide a brief overview of the main results achieved. In particular, I will report on the implementation of a high-energy tunable source of ultrashort pulses in the near-IR based on Optical Parametric Amplification (OPA) and I will describe the first demonstration of High-order

Harmonic Generation inside a gas-filled micro-structured photonic device.

The leading technique for high-energy tunable ultra-broadband pulse generation is currently provided by Optical Parametric Amplification (OPA). OPA occurs in suitable nonlinear optical media and involves energy transfer from a high-energy high-frequency beam (called pump) to a low-energy low-frequency beam (called seed). As a result, the energy of the seed pulses can be substantially increased, up to the pump energy level. OPA is a non-resonant process and it can be used for pulse amplification even in those spectral regions that are not covered by lasing media. Within my Ph.D., I worked on the development of a mJ-level source of few-cycle laser pulses tunable in the near-IR. A schematic view of the source is provided in figure 1.a. A 1 kHz Ti:Sapphire front-end laser source delivering 15-mJ 25-fs 800-nm pulses is used for driving the parametric amplifier. A 330- μ J portion of the Ti:Sa beam undergoes spectral broadening inside a Kr-filled Hollow Core Fiber (HCF). Here the laser pulses are compressed down to 10 fs duration. The 10-fs pulses are used for intra-pulse Difference Frequency Generation (DFG)

into a 3-mm-thick BBO crystal. A broadband spectrum of DFG components in the near-IR is thus produced, which extends from 1.3 μ m to 2 μ m. The near-IR signal is subsequently amplified into BBO crystals under a type-II phase-matching configuration. The two amplification stages are pumped respectively with 1-mJ and 6-mJ pump pulses. A portion of the DFG spectrum can be amplified by properly adjusting the phase-matching conditions. This OPA scheme supports CEP-stable near-IR pulses with an energy up to the 1-mJ level and a duration on the 20-fs time scale. For applications related to APG, stability is a fundamental requirement. In order to boost the performances of the amplifier both in terms of energy and CEP stability, an innovative closed-loop control system based on adaptive lenses was implemented.

HHG and APG provide the cutting-edge technology in the field of ultrafast spectroscopy. However, their application is currently confined within very advanced laboratories and large laser facilities endowed with powerful ultrafast laser sources and expensive optical systems. On the other hand, photonics is undergoing a fast evolution towards miniaturization, mainly

driven by the advances in micro-machining techniques. Extremely attractive is thus the perspective to miniaturize HHG beamlines and to build on-chip platforms for attosecond science. This would make attosecond and HHG technology more accessible and available for applications in a wide number of fields. In this framework, I worked on a project that aims at achieving HHG from a gas-filled micro-channel buried into a fused silica substrate. By focusing a portion of the Ti:Sa laser output (200 μ J) at the entrance of the capillary, a broadband harmonics spectrum was observed (see figure 2.b) even at very low gas pressures (below 100 mbar). With respect to standard HHG schemes based on gas jets, the channel-based configuration allowed the enhancement of HHG performances both in terms of efficiency and spectral extension. The fused silica device was fabricated through Femtosecond Laser Micromachining followed by chemical etching in HF (figure 2.a) in collaboration with the research group of Politecnico di Milano working on integrated photonics. The results obtained provide the first real demonstration of HHG-based XUV coherent light generation in a miniaturized device. HHG in more complex

micro-structured architectures is currently under investigation, paving the way for future on-chip attosecond experiments.

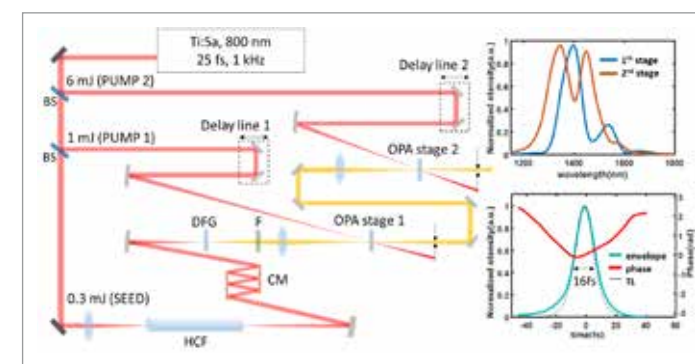


Fig. 1 - Scheme of the OPA source. F, filter. CM, chirped mirror. (b) OPA pulse spectra after the first and second amplification stage. Amplification tuned at 1.4 μ m. (c) Temporal properties of the 1.4- μ m pulses. TL, transform limited.

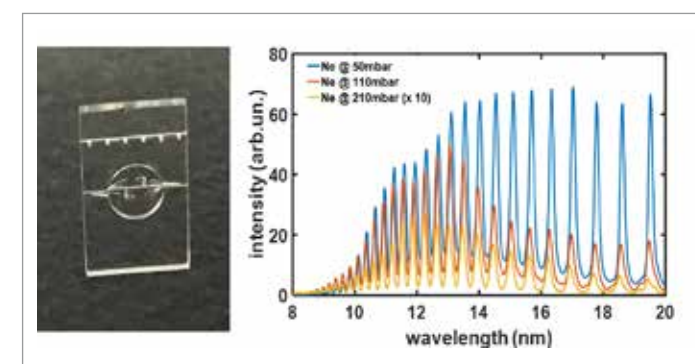


Fig. 2 - Fused silica device endowed with a micro-channel. (b) HHG spectra obtained in Neon gas at different pressures. The yellow spectrum is magnified by a factor 10.

INNOVATIVE TECHNIQUES FOR COHERENT RAMAN MICROSCOPY

Francesco Crisafi - Supervisor: Giulio Cerullo and Dario Polli

Coherent Raman scattering (CRS) is a third-order nonlinear optical microscopy technique for label-free, non-invasive and non-destructive imaging, with growing applications in cellular imaging and disease diagnosis. The widely diffused conventional fluorescence microscopy utilizes a labelling approach of the sample that may cause perturbation of the biological system under study, may limit the capacity of discovery because labels are made for known species and may not be applicable in vivo for potential toxicity related to the adopted markers type. Coherent Raman microscopy, also called vibrational spectroscopic imaging, overcomes these limitations and offers a way to identify molecules by their specific chemical signatures, or "fingerprints", determined by quantized vibrations of the chemical bonds. In coherent Raman microscopy, two narrowband synchronized excitation fields are used, denoted as pump (ω_p) and Stokes (ω_s) and, when the frequency detuning between them ($\omega_p - \omega_s$) matches a Raman-active molecular vibration at frequency Ω , two major processes take place: one is called coherent anti-Stokes Raman scattering (CARS) and the other stimulated Raman scattering (SRS). In the CARS process, a new

frequency is generated at $\omega_{as} = \omega_p + \Omega$, that is called the anti-Stokes frequency; while in SRS, an amplification of the Stokes pulse (SRG, stimulated Raman gain) and an attenuation of the pump pulse (SRL, stimulated Raman loss) is measured. CRS microscopy has been applied in a variety of topics in biology like the study of sclerosis, drug uptake and cancer cells identification (virtual histopathology). In this PhD project a home-built microscope, coupled to a compact fiber-format tunable laser, has been developed in order to build a CRS microscope, with the ultimate goal of studying cancer cells and tissues. In Fig. 1 are displayed the results obtained using CARS microscopy on breast cancer cells treated with an iron depletor; in green is depicted the response of lipids and in blue the response of the medium. Moreover, it's possible to reconstruct the 3D distribution of a chemical content present in the specimen, as it is shown in Fig. 2 for the lipid distribution of two different cell lines (HuH7 and HepaRG). Another goal of the PhD project was to develop new approaches to broadband CRS. Two different methods have been developed, both sharing the capability of retrieving broadband Raman spectra, without the need of a narrowband tunable source.

Chemical content identification of a sample made by two different polymers is obtained by means of their different vibrational spectrum, as it is shown in Fig. 3. This new technique is called Fourier-transform SRS (FT-SRS) and utilizes a special interferometer in the detection chain to retrieve, pixel-by-pixel, the broadband Raman spectrum of the sample. A second broadband SRS technique developed during this PhD project is called photonic time-stretch SRS (PTS-SRS), which exploits the time-stretch dispersive Fourier-transform to obtain broadband vibrational spectra of the sample under study.

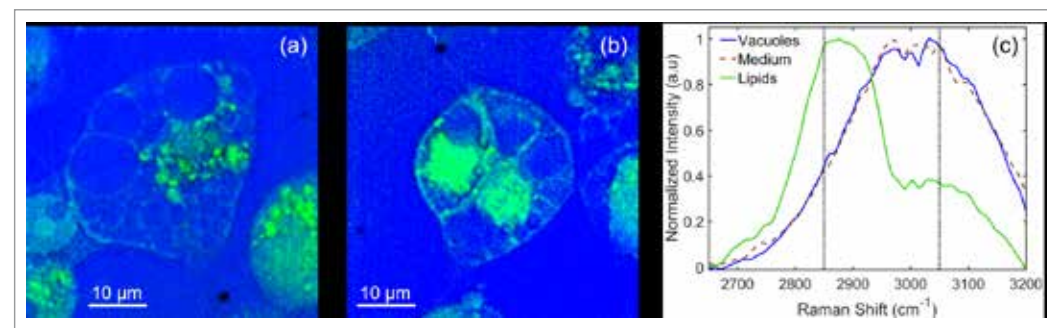


Fig. 1 - CARS composite image collected with the home-made microscope. (a)-(b) Breast cancer cells treated with an iron depletor molecule, where in green is highlighted the response of the lipids at 2850 cm^{-1} (vertical dotted line in (c) on the left) and in blue the response of the medium buffer at 3050 cm^{-1} (vertical dotted line in (c) on the right). (c) Spectra collected in the lipid rich region (green curve), in the medium outside the cells (brown dashed curve) and in the vacuoles present inside the cells (blue solid curve). Samples prepared by I. Bongarzone of Istituto dei Tumori, Milano.

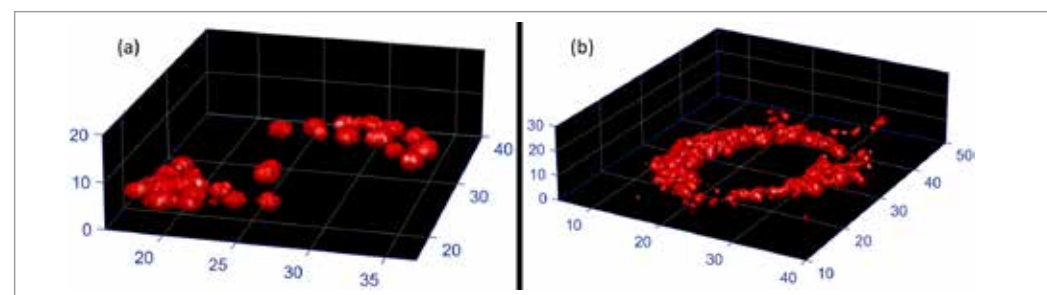


Fig. 2 - 3D distribution of lipids reconstructed with SRS microscopy at 2925 cm^{-1} . (a) HepaRG cell line treated with oleic acid. (b) HuH7 cell line treated with oleic acid. In both images the axis are in μm .

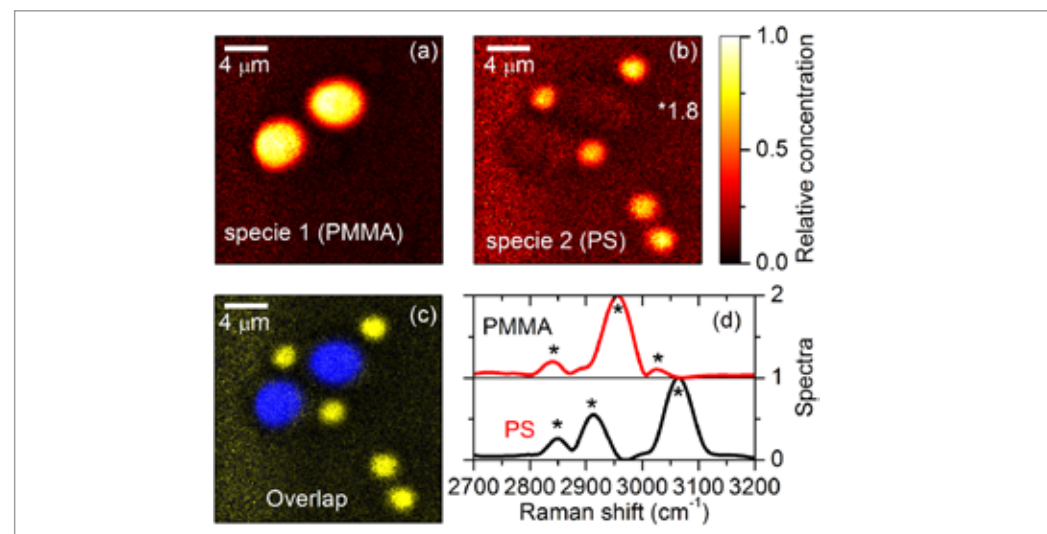


Fig. 3 - FT-SRS images of a mixture of 6- μm and 3- μm diameter beads of polymethyl methacrylate (PMMA) and polystyrene (PS), respectively. (a) PMMA reconstructed distribution. (b) PS reconstructed distribution. (c) Composite image, where in blue is depicted PMMA and in yellow PS. (d) Reconstructed spectra of the two species (PMMA and PS). The stars represent the location of the main peaks obtained by spontaneous Raman reference spectra.

POSITRONIUM FORMATION IN REFLECTION AND TRANSMISSION GEOMETRY FOR GRAVITATIONAL TESTS OF ANTIMATTER

Craig Evans -Supervisor: Rafael Ferragut

Antimatter, the counterpart of ordinary matter, exists in scarce quantities comparing to the abundance of matter in our observable universe. A long journey has been made since the initial postulation by Dirac of the antielectron in 1932 to the current research on antiatomic atoms (antihydrogen, antiprotonic helium) mainly at the Antiproton Decelerator at CERN in Geneva, Switzerland. Physicists around the world are working together search for differences between matter and antimatter. This thesis project was conducted in collaboration with AEgIS (Antimatter Experiment, gravity, Interferometry, Spectroscopy), a CERN based experiment that wants to create antihydrogen through the charge exchange reaction. This reaction involves antiprotons being introduced to laser excited positronium atoms Ps (an electron and positron bound together). They plan to use this method to create an antihydrogen pulsed beam to observe the shift of its trajectory caused by the effect of the Earth's gravitational field. In this way, the idea is to test the matter-antimatter gravitational interaction for the first time. This is a test of the Weak Equivalence Principle, which states that the free fall trajectory of a body does not depend on its composition.

In quantum field theory (QFT), gravity has not yet been included unlike the remaining fundamental interactions (electromagnetic, weak and strong). The measurement of the gravitational acceleration constant g with antimatter could lead to the inclusion of gravity within QFT. The charge exchange reaction requires an efficient source of cold Ps atoms to allow the largest quantity of antihydrogen to be produced. Ps in the triplet state, ortho-positronium (o-Ps), possesses spin 1 (where positron's and electron's spins are parallel) and lives in vacuum an average of 142 ns at the ground state ($n=1$). The antiproton/Ps interaction demands a longer Ps lifetime and a higher n quantum number. A method which can be used is to increase its lifetime by means of laser excitation. With current laser technology, it is possible to excite o-Ps long enough for the charge exchange process to occur. Excitation to Rydberg levels has been undertaken by the AEgIS experiment last year ($n= 1$ to 3 and then $n= 3$ to 15 and 16). For o-Ps production, the widely used method is employing a mesoporous silica target in the reflection geometry. In this geometry, positrons are implanted from one side in this material, form Ps within the pores,

thermalize and exit into vacuum from the same implantation side. It is predicted (through simulation) that changing the geometry to transmission (i.e. Ps exit in the opposite direction of implantation) would benefit this process by increasing the quantity of cold o-Ps emission into vacuum. The VEPAS laboratory of Politecnico di Milano (L-NESS, Como) is involved in the project for the development of these mesoporous silica materials that create a sufficient quantity of Ps inside the pores and then emit them thermalized into vacuum in reflection. The most relevant challenge of this project was to develop for the first time a self-supported target with the ability to emit Ps in the transmission geometry. To accomplish this, it is necessary to overcome an intrinsic difficulty represented by the high fragility of the mesoporous materials to reach a film with the following characteristics: (i) self-supported; (ii) micrometric thickness; (iii) high porosity and low density ($<1 \text{ g/cm}^3$); (v) hydrophobicity and (vi) interconnected pores with nanometric dimensions (3-15 nm). A variety of physical chemistry techniques were incorporated during the development period including spin-coating, liquid-to-air interface, monolith growth,

etc. The more promising film was in the form of the spin-coated films, developed in collaboration with the SmartMatLab (Milan). A sol-gel mixture was administered onto a Si [111] substrate, then spun leaving a thin sol-gel material ready for calcination. The mixture consisted of TEOS ($\text{Si}(\text{OC}_2\text{H}_5)_4$), water (pH= 1.25 with HCl) and ethanol to a molar ratio of (1:5:3.8), a cationic surfactant (CTAB: $\text{CH}_3(\text{CH}_2)_{15} \text{N}^+(\text{CH}_3)_3 \text{Br}^-$) was added to 0.1 CTAB/Si molar ratio and then diluted with ethanol (ratio 1:1). A cylindrical oven was used for the calcination process, removing the unwanted surfactants and leaving a mesoporous silica thin film. The thicknesses were determined to be around 800 nm, measured via HRTEM imaging where it was also observed that a change between morphology at both the bulk/surface and bulk/substrate interfaces, showing an "open" pore structure. These open pores would greatly benefit the o-Ps emission into vacuum. A polystyrene/toluene-based layer was administered onto the substrate prior to the sol-gel, this layer would then be removed via dissolution to release the sol-gel and allow transferal. A laser-irradiated, chemically etched, holed substrate with transmission $\sim 70\%$ was used as the secondary

substrate to allow self-standing to be possible. A continuous positron beam (energy range 0.1 – 20 keV) based at the VEPAS lab was used to characterize these films to find the Ps production properties within the porous materials. The spin-coated material was found to have a high quantity of o-Ps at low implantation energies ($\sim 1 \text{ keV}$), the estimation for the Ps formation yield was $\sim 65\%$, compared with the historically high Ps producing materials (Aerogel $\sim 60\%$). The pore diameter determined to be 3-4 nm (obtained via a positron lifetime measurement) which falls within an acceptable dimension range. The development of the self-supported targets is still on-going but initial tests with these prototypes has been proposed within the AEgIS apparatus at CERN to compare to similar targets. The self-supported target to produce Ps in transmission proposed in this thesis are also relevant for other experiments of fundamental Physics as QUPLAS (QUantum interferometry and gravity with Positrons and LASers) that proposes to form a Ps beam to gravitational tests by means of interferometric techniques. On the other hand, this project also proposed a contribution to AEgIS to work on trapping and manipulation of antiprotons within an electromagnetic trap (Penning

Trap) of a high performance. A direct contribution to the experiment was made to search the ideal cooling and confinement parameters ready for the charge exchange antihydrogen production step.

LEAD HALIDE PEROVSKITE SEMICONDUCTORS: THE ROLE OF MORPHOLOGICAL CONTROL FOR HIGH PERFORMANCE SOLAR CELLS

Marina Gandini - Supervisor: Dr. Annamaria Petrozza

Tri-dimensional lead halide perovskite semiconductors are an emerging solution-processed class of materials that has led to great advances in the performances of solar cells since 2013, and has demonstrated good potential when embodied in light emitting devices and photodetectors. The exceptional opto-electronic properties of these materials, such as the tunable direct band-gap, the extremely high absorption coefficient, the low exciton binding energy, and the balanced ambipolar carrier transport have been extensively studied in the last few years. At the same time, many of the finer details of the device physics remain under debate. In particular, the understanding of the role of structural and chemical defects, and their effects on the properties of devices, has become imperative. Overall, the three-year work highlights the primary properties of the same class of material obtained by various synthetic routes, combining structural and morphological characterizations to the photophysical ones. The thesis work shows a direct comparison between two different approaches to the realization of a perovskite-based thin film. The first one consists in the direct crystallization of the semiconductive material onto a substrate, starting from

precursors solutions, while the second one relies on the deposition of pre-formed high-quality colloidal perovskite-based nanocrystals. The first approach is the most widely used in literature. It consists in the self-organization of ionized precursors dispersed in high boiling point organic solvents, which undergo a crystallization upon thermal treatment. Chemical purity of the precursors, presence of additives, relative humidity, temperature and surface properties of the substrates employed are just few of the parameters that can deeply affect the organization of the perovskite crystalline lattice. In this case, a non-negligible level of unintentional structural and chemical defects is expected, within the bulk and at the interfaces of the crystals. Such defects can introduce localized energy levels that are confined in the band-gap of the semiconductor, creating non-radiative recombination pathways for the photo-generated charge carriers. A reproducible and reliable protocol to fabricate polycrystalline thin film, with different average-crystallite dimensions, is reported. Varying the crystallites mean size, from tens of nanometers to a few

micrometers, it is possible to tune the opto-electronic behaviour of the material, directly influencing the number and the type of electrically-active defect sites. From these results, the existence of a tight tolerance window for the optimal processing parameters of these self-assembled materials clearly emerges. A novel approach is then proposed, consisting in the realization of the solar cell active layer by the deposition of an ink composed by suspended nanoparticles. The ink formulation can be tailored prior to the film formation, meaning that the co-optimization of large-area uniform coverage with a high-quality crystal growth is no longer needed. The results obtained by following this approach are presented in the second part of the thesis. A fully inorganic cesium lead bromide (CsPbBr_3) perovskite has been employed in the study. Since bromide-based compounds exhibit a wide band-gap, around 2.32 eV, these materials can achieve much higher open-circuit values, extending the interest for the applications to multijunction solar cells, visible light-emitting devices and photo-electrochemical cells. A new, fast and one-step-injection synthesis is proposed, leading to the formation of stable colloidal

nanocrystalline perovskite nanoparticles, passivated by organic ligands. The innovative synthesis has the advantages of being a room-temperature and moisture-insensitive process, that employs only low boiling point and less toxic solvents, compared to the ones required in the standard approach. The use of ligands, composed by short alkyl chains, circumvents post-synthesis treatments typical of the longer and bulkier chains usually employed in this field. The passivating nature of the nanocrystal's ligands gives rise to extremely good photo-luminescence properties. The photo-luminescence quantum yield for the colloidal suspension is higher than 75%, and it drops to 35% after the particles have been deposited. The thin film obtained shows an amplified spontaneous emission (ASE) threshold as low as 1.5 mJ/cm^2 , which sets a record for not-passivated inorganic nanostructures. The optical quality observed is close to those of nanocrystals made with high-temperature hot-injection syntheses previously reported in literature. Interestingly, the quantum yield from the films prepared with bulkier ligands are comparable to the ones typically observed from the films here reported, but they remain

non-conductive. Both the quantum yield and the ASE threshold values are indicative of a lower defect density compared to perovskite thin film obtained from standard direct-crystallization approaches. The CsPbBr_3 perovskite inks are then used to fabricate a halide perovskite nanocrystalline-based photovoltaic prototype device. The deposition of highly uniform and complete films has been uniquely facilitated by the use of low-boiling point solvents for the preparation of the colloidal suspension. Sequential deposition cycles enable a fine control over the final active-material thickness. In particular, a layer of $550 \pm 50 \text{ nm}$, corresponding to an optical thickness of more than 1.5 OD, exhibited a power conversion efficiency of 5.4%, which is comparable to the best-performing and fully optimized devices reported so far. The solar cell exhibits short circuit current (J_{SC}) and an open circuit voltage (V_{OC}) values of 5.6 mA/cm^2 and 1.5 V, as well as a fill factor of 0.62. The value for V_{OC} is among the highest reported for perovskite halides, underlying the high quality of the perovskite crystals. For a better understanding of the reference, the calculated ideal maximum V_{OC} and J_{SC} are 2.05 V and 7.78 mA/cm^2 under AM1.5 illumination, considering

a bandgap of about 2.38 eV. Finally, it has to be highlight that this process is fully carried out in ambient air. Moreover, the technique provides electrically stable devices. Finally, a fine analysis over the ligands' role in the device performances has been carried out. At the same time, the correlation between the nanocrystal size and the figures of merit of the devices has been investigated, highlighting the nanocrystal size-dependence of the current density in the device. The validity of this novel approach has been further demonstrated by successfully applied it to large-area deposition techniques (bar-coating), obtaining working devices with performances comparable to the previously reported ones.

SECOND HARMONIC GENERATION ENHANCEMENT AT THE NANOSCALE USING PLASMONIC AND PHOTONIC ANTENNAS

Lavinia Ghirardini - Supervisor: Michele Celebrano

The field of Nonlinear Optics was born together with laser technology back in the 1960s, and since then it has been employed in a wide variety of applications. Frequency conversion has been used in photonics, for laser spectral control and ultrashort laser pulses generation for research and industry purposes. The peculiar dependence of the different nonlinear processes on either the bulk or the surface properties of objects together with their selection rules has been exploited as a tool for the characterization of crystalline solids in material science as well as for the study of dynamics at interfaces and in advanced bioimaging techniques. More recently, nonlinear optics has been employed for the generation of entangled photon pairs, which are the information basis of quantum computing and quantum cryptography applications. Finally, following the development of nanotechnology applications for medicine, nonlinear optical processes has been implemented in the development of a new generation of sensitive and efficient biosensors and in theranostics applications. The technological challenge for these new applications is the pursuit for light-matter interaction enhancement in order to push the limit toward nanoscale integration,

an aspect which has strongly stimulated research and industry activities during the 20th-century. In fact, optical on-chip integration is a fundamental technological aspect in fields like quantum optics, biotechnology and nanomedicine, to be able to generate and manipulate nonlinear processes at the nanoscale to allow the birth of the next-generation technology. However, the major issue in down-scaling the basic nonlinear elements to the microprocessor level is the inherent weakness of nonlinear optical processes. In macroscopic media, it is possible to exploit the coherent interference of the nonlinear sources inside the material to build up a detectable signal, by satisfying the so-called phase matching conditions in the medium. This, however, is not possible with nanostructured platforms that aim at confining nonlinear optics beyond the diffraction limit. For this reason, the scientific community had to identify alternative methods to increase the efficiency of nonlinear processes at the nanoscale. To this purpose, a successful approach turned out to be the exploitation of the intense field enhancements produced by photonic and plasmonic resonances in nanostructures. In my thesis, I introduce the

two main types of nanoscale resonators used for efficient nonlinear generation at the nanoscale, metals and dielectrics, comparing their enhancement mechanisms and requirements. In particular, I will focus on the design and characterization of such nanoresonators in order to optimize their efficiency for the process of Second Harmonic Generation (SHG). SHG, consists in the simultaneous absorption of two photons from the same pump beam followed by the emission of a photon at twice the fundamental pump frequency. Being one of the lowest-order nonlinearities, SHG is one of the most efficient nonlinear optical processes that can be studied. Finally, it can be implemented in a number of applications as it will be shown in the course of this thesis, from holograms to infra-red vision or biosensing, but it can also be used as a paradigm for the optimization of the other even-order nonlinear processes. My PhD thesis presents nonlinear optics in metals sustaining localized surface plasmon resonances, and describe the design, fabrication and characterization of arrays of non-centrosymmetric gold nanoantennas. These resonators feature a double resonant behavior, designed to enhance both absorption at the pump

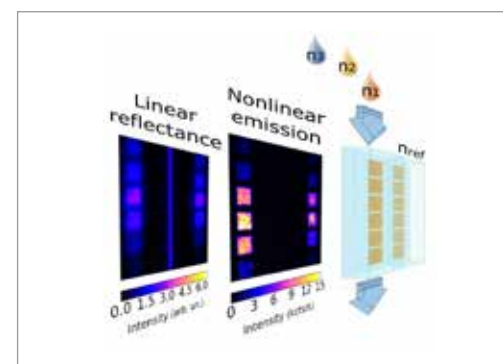


Fig. 1 - Sketch of the prototypical plasmon-assisted nonlinear sensing platform. The microfluidic channel includes a set of antenna arrays, while their reference copy is kept at a constant refractive index n_{ref} , encapsulated under the microfluidic chip. The intensity of the nonlinear emission and of the linear reflectance from the antennas within the channel will depend on the refractive index of the solution flow through the microfluidic system.

frequency and emission at the second harmonic wavelength, and an optimal spatial mode overlap to increase the nonlinear conversion efficiency. I describe the fabrication of a prototypical plasmon-assisted nonlinear sensing device realized by integrating our nanoscale platform with a microfluidic chip. In particular, I characterize and compare its linear and nonlinear refractometric sensing performances, contextualizing it into the frame of contemporary linear and nonlinear plasmonic sensing. Metals working at optical frequencies, however, are known to have high ohmic losses, which can be a limitation for some applications in terms of pump power, conversion efficiency, and heating of adjacent biochemical species. Moreover, even-order nonlinear processes in centrosymmetric materials like plasmonic metals are constrained by stringent symmetry requirements. For this reason,

in the last decade, many efforts have been also dedicated to the study dielectric nanostructures sustaining Mie-type resonances that can act as virtually lossless optical nanocavities. In this regard, my thesis also presents the design, fabrication and characterization of a III-V platform made of $Al_{0.18}Ga_{0.82}As$ nanocylinders on a high-refractive-index AlOx substrate. This material has an intrinsically non-centrosymmetric crystal lattice that, together with its band structure, makes it an ideal candidate to efficiently pump SHG at the telecom wavelength. The Second Harmonic emission properties of this platform will be fully characterized as a function of the resonators geometry. In order to be marketable, however, these platforms need to reach efficiencies comparable to those of currently used emitters, in the order of 10^{-3} . This $Al_{0.18}Ga_{0.82}As$ nanostructures, despite being the best-performing SHG platform



Fig. 2 - Sketch of the studied $Al_{0.18}Ga_{0.82}As$ -on- $AlOx$ platform. It consists of a GaAs wafer with $Al_{0.18}Ga_{0.82}As$ cylinders on top of a 1- μm -thick aluminum oxide (AlOx) layer. The resonators are 400 nm high, with radii varying between 180 nm and 220 nm, placed at a distance of 3 μm from each other

so far demonstrated, present a radiation directionality that does not couple efficiently with standard collection systems. Consequently, various strategies have been theoretically investigated in order to maximize the collection efficiency of this platform. To this purpose, my PhD thesis presents the experimental characterization of two of these techniques. The investigated schemes allow to actively reshape and control the nonlinear radiation pattern from our dielectric resonators, both in a static and in a dynamic configuration. This SHG radiation control offers not only the possibility to maximize the collection efficiency but paves also the way for the realization of active components like, for example, single antennas for holography and nano-goniometers for light, which can further expand the range of possible applications of integrated nonlinear nanophotonic.

ELECTRONIC AND MAGNETIC COUPLING OF OXIDES AND ORGANIC FILMS TO A FERROMAGNETIC SURFACE

Dario Giannotti - Supervisor: Alberto Brambilla

During the last decade, the progress in microscopy techniques and the improvement in epitaxial growth have made possible the development of new micro and nano-devices. As the size becomes, small the study and characterization of surfaces and interfaces become crucial to determine devices properties and to envisage new ones. About this, the discovery of giant magnetoresistance in 1988 and the possibility to engineer heterostructure with magnetic character have made the birth of spintronic possible. In this field both oxide-ferromagnetic (FM) metal and organic-FM metal interfaces have been receiving much attention. On the one hand, the systems obtained by coupling an anti-ferromagnetic (AF) thin-film with a FM substrate find applications in devices based on exchange bias, such as spin valves or magnetic memories. On the other hand, thanks to the long electron spin coherence and weak spin-orbit coupling, organic semiconductors (OS) forming hybridized magnetic interfaces with FM metals are promising candidates for spintronic applications. Moreover, the formation of layered structures with an ultra-thin oxide film at the OS/FM interface allowed to develop new properties.

Thanks to the use of scanning tunneling microscopy (STM) and different spectroscopy techniques, I have pursued the following principal aims of my PhD research activity. First the achievement of a sharp interface between CoO (AF) and Fe (FM), using the so called reactive deposition (deposition of metal at $\sim 10^{-6}$ mbar pressure of oxygen in ultrahigh vacuum conditions), in order to investigate the early stage of oxidation and to set the magnetic properties of a thin oxide film. Second, to investigate how both the electronic and the magnetic coupling between C_{60} fullerene and a metallic substrate change if a single layer of oxide is present at the interface among the two materials. Due to the high reactivity of metal surfaces with oxygen, the growth of a well-defined oxide film on a FM substrate is an important challenge to confront with. To avoid Fe oxidation, before the reactive deposition we grow a buffer-layers of metallic Co on Fe. This has also allowed us to realize a preliminary post-oxidation study of the surface. Figure 1a displays an STM image of 5 monolayer (ML) of Co on Fe(001) after a dosing of 7 L ($1 \text{ L} = 1.3 \times 10^{-6} \text{ mbar}\cdot\text{s}$) of pure O_2 . It is possible to see a homogeneous nucleation of oxide islands, which have defects

(dark spots) inside (Figures 1b). After having checked the absence of Fe oxides on the surface, we have grown CoO films on such substrates. Figure 1c shows a STM image of 6.4 ML of CoO on Co/Fe(001). The surface is well-ordered, with regular spaced CoO islands. The presence of a network of misfit dislocations at the interface works as a template for the nano-structuration of CoO, formed by square mounds with 25 nm of lateral size. Figure 1d reports magnetic hysteresis loops measured on such samples, realized with the geometry sketched above. Such results demonstrate the breaking of the fourfold magnetic symmetry of Fe surface, which is only obtained in presence of the buffer layer. Regarding the OS/FM interfaces we explored the morphology, electronic and magnetic coupling of C_{60} on two different substrate: Fe (001)- $p(1 \times 1)O$ and $Cr_4O_5/Fe(001)$. The former is featured by the presence of a single layer of oxygen on top on Fe surface in the hollow site of Fe lattice, resulting in a FeO atomic layer on the surface. The latter is a single layer of Cr oxide on Fe(001), characterized by a regular array of Cr vacancies that results in a $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ reconstruction with respect to the substrate lattice. Previous investigations show that this

layer is FM with a magnetization vector antiparallel with respect to Fe. Figure 2a and 2b display the STM topography for the two-different substrate. By calculating the fast Fourier transformation (FFT) of the image (insert of Fig.2a) we can observe that on C_{60} arrange in hexagonal islands on Fe (001)- $p(1 \times 1)O$, without any preferential axis (developing multiple domains). On the other hand in the low energy electron diffraction (LEED) pattern for $C_{60}/Cr_4O_5/Fe(001)$ (insert of Fig.2b) only two domains are present, rotated by 90° with respect to each other. The magnetic character of the two samples has been investigated by calculating X-ray magnetic circular dichroism (XMCD) spectra from X-ray adsorption spectroscopy (XAS) measurements collected at the Elettra synchrotron, which are shown in Figure 2c and 2d for the two cases. While on Fe (001)- $p(1 \times 1)O$, the XMCD signal is about

5% of the XAS signal, on $Cr_4O_5/Fe(001)$ it increase to about 12%, suggesting that the magnetic thin oxide layer induces a remarkable magnetic moment on fullerene. In conclusion, during my doctoral work, I have reached two achievements: first I have obtained well-defined CoO/Fe interfaces which present unique magnetic properties. Second, thanks to the employment of an two dimensional oxides, we have shown that it is possible to enhance the magnetic moment at the C_{60}/Fe interface. Figure 1: (a) Constant-current STM image of 5 ML Co- $p(1 \times 1)O$ after exposure to 7 L of O_2 . The size is $200 \times 200 \text{ nm}^2$ and the tunneling parameters are $I = 1 \text{ nA}$ and $V = 1 \text{ V}$. (b) Atomically resolved image of CoO island. (c) STM image ($200 \times 200 \text{ nm}^2$) of 6.5 ML CoO film ($V = -3 \text{ V}$; $I = 10 \text{ pA}$), The line profile below is measured along the dashed line. (d) Hysteresis loops of the in-plane magnetization components

(parallel and perpendicular to the magnetic field), taken on a sample with 25 ML CoO. Figure 2: STM images of C_{60} deposited on (a) Fe (001)- $p(1 \times 1)O$ and (b) $Cr_4O_5/Fe(001)$. The insert in (a) shows the FFT of the image, while the insert in (b) display the LEED pattern (22 eV). In (c) and (d) the red and the black lines are the XAS spectra at the $C \text{ K}_1$ edge, for left and right circular polarization respectively. The corresponding XMCD spectra (blue) are reported below.

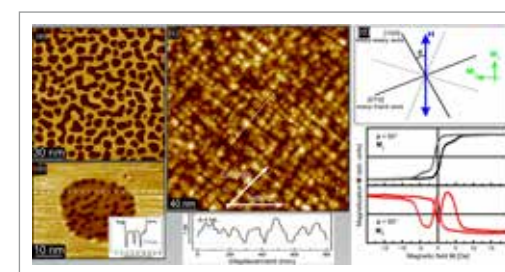


Fig. 1 - (a) Constant-current STM image of 5 ML Co- $p(1 \times 1)O$ after exposure to 7 L of O_2 . The size is $200 \times 200 \text{ nm}^2$ and the tunneling parameters are $I = 1 \text{ nA}$ and $V = 1 \text{ V}$. (b) Atomically resolved image of CoO island. (c) STM image ($200 \times 200 \text{ nm}^2$) of 6.5 ML CoO film ($V = -3 \text{ V}$; $I = 10 \text{ pA}$), The line profile below is measured along the dashed line. (d) Hysteresis loops of the in-plane magnetization components (parallel and perpendicular to the magnetic field), taken on a sample with 25 ML CoO.

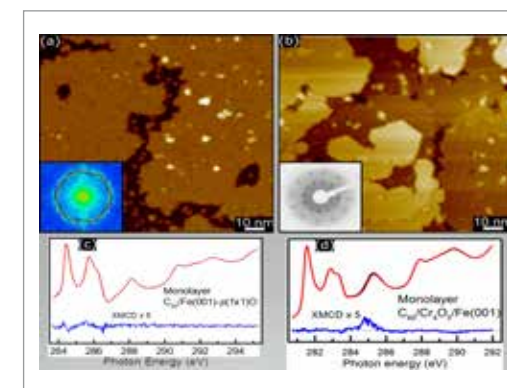


Fig. 2 - STM images of C_{60} deposited on (a) Fe (001)- $p(1 \times 1)O$ and (b) $Cr_4O_5/Fe(001)$. The insert in (a) shows the FFT of the image, while the insert in (b) display the LEED pattern (22 eV). In (c) and (d) the red and the black lines are the XAS spectra at the $C \text{ K}_1$ edge, for left and right circular polarization respectively. The corresponding XMCD spectra (blue) are reported below.

COMB-ASSISTED CAVITY-ENHANCED MOLECULAR SPECTROSCOPY AT HIGH-PRECISION AND SENSITIVITY

Riccardo Gotti - Supervisor: Dr. Davide Gatti

Tutor: Prof. Marco Marangoni

Abstract: The thesis focuses on the development and application of two near-infrared spectrometers operating with extreme sensitivity and precision on molecular samples in the gas phase at very low pressures. The sensitivity is achieved by introducing the gas in an optical cavity with very high finesse, extending the effective absorption path length much beyond the geometrical length. The precision as well as an absolute calibration of the optical frequency axis is obtained by referring the probe laser to an optical frequency comb. The latter is a revolutionary tool for spectroscopy awarded by the Nobel prize for Physics in 2005, which acts as a ruler for optical frequencies and allows them to be measured against primary references.

The motivation for the realization of such a type of spectrometers derives from several elements: the sensitivity enables the measurement of absorption profiles with very high signal to noise ratio even on relatively weak overtone lines in the near-infrared; the comb-calibrated frequency axis allows to test the correspondence of the measured profiles against collisional physics models and to extract high-quality spectroscopic parameters,

such as Doppler width and line centre frequency; a pressure regime at the few-Pascal level, accessible through a highly sensitive spectrometer, may be exploited for the saturation of the absorption, with the emergence of extremely narrow spectral features such as Lamb dips that are of major interest to extract line centre frequencies and thus energy levels with ultimate precision.

A first spectrometer has been developed to maximize the intra-cavity power and achieve the conditions for Doppler-free spectroscopy in a saturation regime at low pressures. The system relies on a simple optical lay-out and covers a broad range, from 1.5 to 1.63 μm , which makes it suitable to access a large variety of transitions for several molecules of interest. As compared to competing spectrometers, key features are the high intra-cavity field intensity, which enables the saturation of lines with a very weak electric-dipole-moment, and the acquisition of the entire Lamb dip profile against an absolute frequency scale, which gives the chance for a deeper understanding of molecular line-shapes in a saturated regime. From a technological point of view, our spectrometer has

been the first relying on a single feedback loop to force the coincidence between the probe laser frequency and the cavity resonance. The locking has been obtained in a Pound-Drever-Hall regime using an optical single sideband modulator as an ultra-fast high-dynamic-range frequency actuator. Thanks to a feedback bandwidth of about 5 MHz, one of the highest reported so far, and to a capture range of the loop of 150 MHz, the probe laser remains steadily and efficiently locked to the 3-kHz-large cavity resonances even when the cavity length is scanned over sub-Doppler features. The locking is tight enough to quench the fluctuations of the transmitted power to less than 0.1% and to read out the gas absorption in a purely DC regime with a signal-to-noise ratio of about 1000 over the second-time-scale.

The spectrometer revealed a powerful tool to acquire Lamb dips: these are typically acquired by repeated scans over 10 MHz, with 100 spectral points and a measurement time of 2 s per scan. Such a low measurement time is beneficial for the low-pressure regime explored, as it avoids any degradation of the experimental conditions due to cavity leakage. The signal-to-noise ratio by

averaging over 200 s approaches 10000, which is equivalent to a sensitivity of $2.5 \cdot 10^{-11} \text{ cm}^{-1}$. In the frequency domain, thanks to the referencing of the probe laser to an optical frequency comb, this translates into an accuracy on the line-centre frequency of $8 \cdot 10^{-12}$ (1.5 kHz), which is comparable to the best values reported so far. The accuracy has been tested on well-studied acetylene lines of the 10100-00000 band, used as references in the Telecommunication band and reported by several metrological institutes, whereas the sensitivity and saturation capability have been checked on the P15e line of the 01120-00000 band, featuring a line intensity and an electric-dipole-moment among the weakest ever observed. The second spectrometer has been engineered to minimize the acquisition time and optimize the signal-to-noise ratio of Doppler broadened spectra, again at low pressures. The aim is to infer from a proper fitting of those spectra a highly accurate value of their Doppler width and in turn of the absolute gas temperature: this is the underlying concept of Doppler-broadening thermometry, which is a primary method of gas thermometry recognized by the International Committee

for Weights and Measures for the determination of the thermodynamic temperature of atomic or molecular gases. The development of such a primary gas method acquires a particular relevance in view of the forthcoming redefinition of the Boltzmann constant in 2018. The spectrometer is based on the cavity-ring-down-spectroscopy technique, largely employed for the acquisition of Doppler-broadened spectra in the linear absorption regime. It deduces the absorption coefficient by a comparative measurement of the photon cavity lifetime in the presence and in the absence of the gas sample. As it relies on a decay-time measurement it is intrinsically independent of the laser intensity noise. Cavity-ring-down spectroscopy does not require a tight locking of the laser to the cavity; it has been here implemented with an innovative frequency scan procedure that exploits the large bandwidth of an optical single sideband modulator to probe the gas absorption over 3200 spectral points with a measurement time as low as 6 s. With such a fast measurement, the spectrometer does not suffer from any degradation due to the drifting of experimental conditions and exhibits a state-of-the-art

sensitivity of $4.4 \cdot 10^{-12} \text{ cm}^{-1}$ at 1 s. As the frequency of the probe laser remains calibrated against a frequency comb during the spectral scans, the spectrometer lends itself to the acquisition of high quality spectra on both the horizontal and vertical axis of the measurement. It has been applied to the investigation of an isolated near-infrared line of carbon dioxide, the P12e line of the 30012-00001 band, at thermodynamic equilibrium in the pressure range from 1 to 7 Pa. A refined multiple fitting procedure applied to an ensemble of 35 spectra allowed the determination of the gas temperature with an unprecedented level of accuracy and precision, with a global uncertainty of 14 parts over 10^6 in a measurement time of almost 5 hours, ranking the system at the first place among optical methods. Our approach paves the way towards the optical determination of the thermodynamic temperature with a global uncertainty of 1 part over 10^6 , which is an ultimate target for primary thermometry methods.

PLASMONIC AND STRAIN-ENGINEERING IN GE-BASED DEVICES FOR NIR PHOTODETECTION

Mario Lodari - Supervisor: Monica Bollani

Silicon compatible semiconductors are a sought achievement in the near and mid infrared (NIR-MIR) application field. Nowadays, the main goal in optoelectronics is to integrate in the mass production Si-based industry a coherent light emitter and a photodetector. To add such features in integrated circuits and in communication systems, manufacturers adopted group III-V alloys devices and complex integration schemes, including expensive wafer and/or device bonding processes. Even though replacement materials have been developed, investors and manufacturers are reluctant to adopt new technologies that are not fully compatible with the Si complementary metal-oxide-semiconductor (CMOS) technology because of the costs. Telecom applications, and optical interconnect as well, exploit silica glass-based optical fibers which have two transparency windows in the IR region at 1.3 and 1.55 μm . Working at these λ , in long distances communications the transmitted signals undergo a lower attenuation (dB/km) reducing the number of optical repeaters needed. On the other hand, in the short distance systems, the signal to noise ratio (SNR) can be kept at higher values. Because of its band structure, Si has two main drawbacks in

optoelectronics: the indirect bandgap, and its 1.11 eV height. The former results in a poor light emission efficiency, the latter stops the optical absorption at 1.1 μm . For these reasons, III-V semiconductors have been adopted in telecommunication and are now a well-established technology in both light emission and detection. Concerning the light absorption applications, the Ge is a solid, valuable and reliable material on which several devices have been demonstrated and based on: photodiodes, single photon avalanche diodes (SPAD), integrated waveguides, optical modulators and so on. In addition to its full compatibility and high charge carriers mobility, Ge offers interesting optical properties despite it being an indirect bandgap semiconductor. In fact, at higher energy with respect to the 0.66 eV indirect fundamental bandgap it also displays a 0.8 eV direct bandgap. Therefore, a Ge-based photodetector extends the Si optical absorption further in the IR up to 1.55 and 1.8 μm where the direct and the indirect band edges lie. Making a CMOS compatible NIR photodetector feasible, Ge is an eligible material for the telecommunication range. This thesis work has been focused in the achievement of a reliable approach that can

provide a modification into the already known and exploited Ge absorption characteristic, tailoring its response. I took advantage of two different approaches: plasmonics and strain engineering, to enhance its responsivity at a specific λ or pushing the upper absorption limit at higher λ respectively. The former has been used to propose a Ge-based photodetector for sensing applications in the 1.3 – 1.5 μm range, the latter to propose an approach to shift and extend the Ge light absorption at higher wavelengths. The thesis is divided in two parts. The first one is focused on the plasmonic enhanced photodetector, while the second one on the strain engineering for NIR and MIR photodetection. Localized and/or propagating surface plasmon polaritons (SPPs) have already been successfully used to enhance the performance of photodetectors. Sensing is the field of choice for plasmonic applications. It permits to study, detect and characterize small analytes even at very low concentrations thanks to resonantly-enhanced and highly localized electromagnetic fields. Therefore, in the first part of this dissertation, I used Metal-Semiconductor-Metal (MSM) photodetectors because of their

high responsivity and high-speed response in addition to a straightforward fabrication. Furthermore, their planar design makes possible to design the metallic contacts to integrate plasmonic effects by acting on their shape, spacing and aspect ratio. A suitable periodic design turns the interdigitated finger-like contacts of a standard MSM into a plasmonic grating, tailoring the light spectrum that reaches the underlying Ge and boosting the photodetector sensitivity at a specific resonant wavelength. With the support of a numerical simulation tool, different geometries and contact characteristics have been studied to pursue a resonant responsivity enhancement. Electron beam lithography (EBL) and electron beam evaporation techniques have been used to fabricate the samples, which have been characterized via two probes electrical measurements and via a lock-in technique for photocurrent detection. Depending on the considered MSM configuration, high gain factors can be achieved from a simulation point of view. Experimentally, a plasmonic enhanced interdigitated MSM for NIR photodetection has been proved in good agreement with the reported simulations. In a device development, or in general when an electrical connection is needed, one important and fundamental aspect is the nature and the quality of the metal-semiconductor interface. A Schottky contact can be used to significantly lower the baseline signal flowing through the device due to the presence of an energy

barrier. In photodetection, a small background dark current improves the SNR and the sensitivity of a device. Therefore, in this thesis work I adopted Schottky Ge-metal contacts. Optical lithography and e-beam evaporation have been used to test different metals, to analyse both the height and the reproducibility of the Schottky barrier. In addition, different surface preparation cleanings have been used in order to point-out their role in the contact characteristics. A stable, reproducible and feasible Schottky contact has been found. Aiming to a sensing application, it is fundamental to set a detection mechanism. It should offer a reliable method to modify the device optical response and guarantee the selectivity to the desired analyte. Because of the peculiarity of the chosen photodetectors, the device surface can be grafted to trap a desired analyte, inducing local variation in the transmitted light toward the Ge active medium. When the analyte is trapped, shadowing mechanisms enable the detection of the photocurrent signal. Numerical simulations have been performed to investigate the role of the grafting layer. Experimentally, I also report the Ge surface functionalization by a thermally activated wet approach. This is a low-cost technique that ensure a good sample coverage, although it requires a long process time. Regarding the second part of this dissertation, a method to induce high uniaxial and biaxial tensile strain values is proposed and demonstrated. Strain engineering is a well-known

approach to modify and boost a material electrical properties, such as electron and/or hole mobility. Furthermore, modifying a material band structure it is possible to tune its bandgap for optical applications. If a tensile strain is applied to the Ge, the result is a bandgap lowering and when some threshold values are exceeded it can be turned into a direct bandgap semiconductor. However, in this thesis work the focus has been set on the induction of a smaller bandgap in Ge. In fact, a smaller band gap leads to a more efficient light absorption at higher wavelengths where a CMOS compatible absorber still misses. For this purpose, I propose a top-down approach to induce tensile strain in suspended Ge membranes by the forces produced from SiGe stressors. On a Si(001) substrate, a coherent epitaxial SiGe film has been grown on a relaxed Ge films from which SiGe micro- and nano-structures have been designed and fabricated to achieve high strain in large suspended Ge areas. EBL, dry and wet etching were used, while x-ray diffraction (XRD) and uRaman have been used to investigate the initial and achieved strain state, respectively.

STUDY, DESIGN AND DEVELOPMENT OF NOVEL DEVICES AND METHODS FOR RAMAN SPECTROSCOPY

Sara Mosca - Supervisor: Prof. Gianluca Valentini

Raman spectroscopy is used for characterizing and analyzing a wide range of materials. The technique is based on the analysis of emitted photons that undergo a small energy shift with respect to the incident radiation. This shift carries information about the vibrational energy levels of the analyzed system leading to the possible identification of its chemical composition. The main framework of this work resides in the study and application of Raman spectroscopy as a non-invasive tool for chemical analysis in different fields. This thesis reports the development of new solutions for performing Raman Spectroscopy that exploit different experimental configurations and theoretical calculations of Raman scattering. The first part of the dissertation proposes and validates a new Raman device that was designed in order to perform a stand-off mapping of an area of square centimeters at a working distance of approximately 30 cm. This device is remarkably suitable for in situ analysis of artworks. Fig.1 shows the results of the analysis on a painting. On the basis of the Raman spectrum (fig.1.e) and the spatial distribution of the main Raman components (fig.1b-c) it was possible to identify cinnabar, gypsum and carbon black as the main pigments

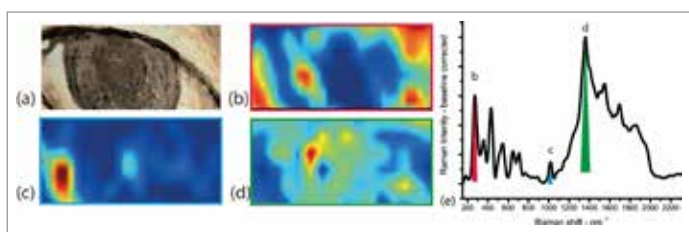


Fig. 1 - (a) Color image of a paint detail analyzed with the Raman mapping device; (b-d) Spatial distribution of the most significant Raman bands in the dataset; (b) 252 cm⁻¹ (c) 1007 cm⁻¹ (d) 1313 cm⁻¹ (e) Mean Raman spectrum of the analyzed detail. Red, green and blue full fill indicates peak area used for extract Raman maps.

used for pink, white and brown hue, respectively. The synergic combination of macro-Raman mapping and complementary spectroscopic imaging techniques can easily reveal material composition in complex mixtures. This is particularly useful in conservation science.

The second part of the dissertation is focused on the detection of Raman signals in Biological tissues. A new technique named Frequency Offset Raman Spectroscopy (FORS) was proposed. FORS takes advantage of the variation of the optical properties, scattering (μ_s') and absorption (μ_a) over multiple wavelengths in order to probe different depths within the tissue. The operating principle is shown in Fig.2 (a) with reference to a two layer sample mimicking the optical properties of different

biological tissues. At low excitation wavelength (700nm) the medium has high value of μ_a and μ_s' , which precludes photons from reaching the deep layer, so that the Raman signal is dominated by the top layer (fig.2b. blue line). Upon excitation at higher wavelength (808 nm), in correspondence of lower μ_a and μ_s' values, photons can propagate deeper so that the contribution of the bottom layer increases (fig.2b.red line). FORS was tested on solid phantoms and resulted a valid alternative respect to the existing techniques, promising a good viability in the Biomedical field.

The last part of the dissertation is on the application of Raman spectroscopy combined with Density Functional Theory (DFT) calculation for the characterization of a conductive polythiophene system with a 3D-protection

architecture. The π -conjugation of the polymer backbones was investigated as was its relation to the order of the main chain in the case of fully encapsulated polymer (i.e defect free in fig.3) compared with a defect co-polymers system characterized by some not-encapsulated thiophene units (i.e defect unit). In conjugated organic molecule the most significant Raman frequencies, expressed in term of the collective C=C/C-C stretching (i.e **R** mode), are characteristic of the bond length alternation structure and for that reason the bands are a marker of the π -conjugation. Experimental Raman spectra supported by DFT calculation (fig.3) demonstrates that the presence of defect units introduces distortion that leads to a decrease of π -conjugation with the appearance of a new **R** mode at higher frequency.

In conclusion, thanks to the application of Raman spectroscopy from both experimental and theoretical perspective, the advantages and limitations of this spectroscopic technique for characterizing a great variety of materials are explored and range from precious artworks to organic molecules with promising moieties for optoelectronic applications.

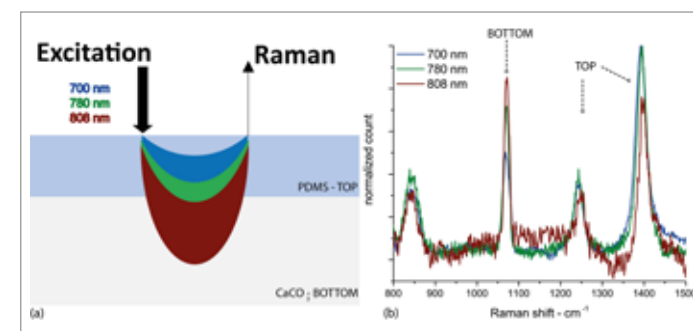


Fig. 2 - (a) Principles of FORS measurement. (b) FORS-Raman spectra at different excitation wavelength of the bi-layer phantom (Bottom=Polydimethylsiloxane, Top=CaCO₃.)

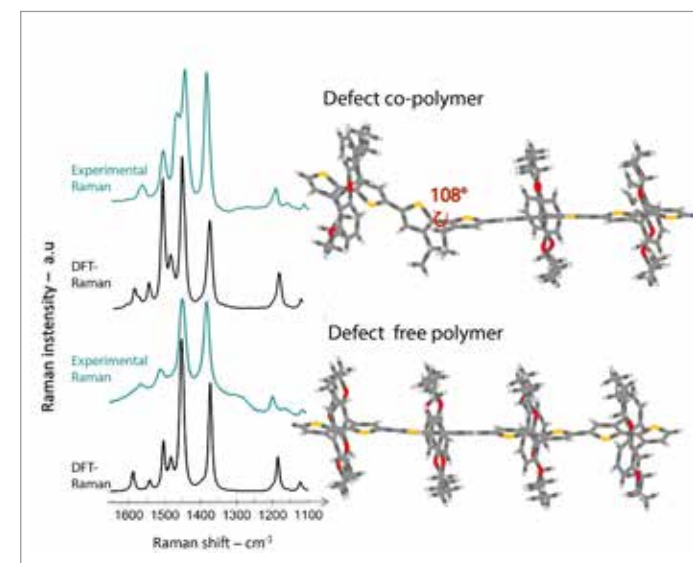


Fig. 3 - Experimental (dark cyan line) and DFT Raman spectra (black line) of defect free polymer (bottom) and defect-co-polymer (top). On the right, the optimized structure of the two system calculated with Gaussian09 using the B3LYP functional and 6-31G basis set.**

NONLINEAR LIGHT-MATTER INTERACTIONS IN LEAD HALIDE PEROVSKITES AND THE ROLE OF CRYSTAL STRUCTURE

Stefanie Claudia Neutzner - Supervisor: Dr. Annamaria Petrozza

Semiconductors are the building blocks of the current technological development, influencing practically all aspects of our modern society. Their success is based on their diversity and therefore the potential to engineer their optoelectronic and structural properties. In several technological fields, organic semiconductors started to supersede inorganic materials, due to excellent luminescence properties, low temperature processability and flexibility of their chemistry allowing easy adjustment of the material to meet certain requirements. On the other hand, they exhibit several drawbacks, including poor thermal and mechanical stability and restricted carrier mobilities at room temperature. In the effort to overcome these limitations and to combine the desired characteristics of organic and inorganic materials in a single molecular-scale compound, hybrid semiconductors have been extensively studied with the goal to compose systems with superior electro-optical properties.

One class of hybrid materials in particular, the hybrid lead halide perovskites, has drawn global attention of the scientific community by virtue of the success as active material in photovoltaic devices, with

performances exceeding 20% and demonstrations of perovskite based electro-luminescent and lasing devices. This class of materials can be self-assembled by simple chemical deposition of the constituent compounds which permits fine-tuning of the electro-optical properties, promising for a broad variety of applications. Nevertheless, several challenges have to be addressed to exploit their full potential. Owing to their nature of forming a relatively soft ionic crystal structure, hybrid perovskites are intrinsically complex systems and extremely sensitive to processing parameters. Structural disorder, various interactions between the organic and inorganic constituents and the resulting rich defect landscape affect charge transport and excitonic effects and determine their distinct electro-optical properties.

In the present thesis we investigate the light-matter interaction of hybrid perovskites using a variety of nonlinear spectroscopic methods with the objective to expand the photophysical understanding of the structure-function relationship in these materials and to provide useful information for material optimization to expedite perovskite based technologies. The work can be divided into

two parts corresponding to the material class under investigation:

- i) Ultrafast dynamics and optical nonlinearities in three dimensional hybrid lead halide perovskites
- ii) The role of crystal structure in two dimensional hybrid lead halide perovskite systems and excitonic many body effects

The main parts are summarized as followed.

Nonlinearities in the light emission characteristics of lead halide perovskites and the role of defects

Non-radiative processes like carrier trapping within intra-gap defect states or multi-particle Auger recombination form the dominant loss-channels in optoelectronic materials limiting photovoltaic and light emission efficiencies and result in nonlinearities in the photoluminescence characteristics of a material.

We use **Excitation Correlation Photo-Luminescence (ECPL)** spectroscopy to study representative lead bromide perovskite systems exhibiting different photoluminescence efficiencies. In contrast to traditional transient photoluminescence spectroscopy, we excite the materials with two pump beams, modulated at different frequencies and use a

heterodyne detection scheme to extract solely the nonlinear part of the photoluminescence due to population mixing. We exploit the superior sensitivity of this method to identify the nature and energetics of trap states in lead bromide perovskites and to complement the current Shockley-Read Hall formalism employed to describe the carrier dynamics in these materials. The technique directly reveals the thresholds between different competing nonlinear processes and constitutes a valuable tool to provide guidelines for material engineering.

Ultrafast dynamics and amplified spontaneous emission at the structural phase transition of hybrid lead iodide perovskites

In this part we specifically address the high excitation density regime in lead iodide perovskites. Polycrystalline MAPbI₃ films undergo an incomplete structural phase transition from the tetragonal to orthorhombic crystal structure at low temperatures, leading to a temperature dependent distribution of small tetragonal inclusions within the orthorhombic phase. Although the absorption is dominated by the orthorhombic band edge, the material exhibits an unusual red shifted emission, spectrally located at the position of the room temperature phase. Using transient absorption spectroscopy, we assign this emission behaviour to transfer between the two crystal phases whose dynamics depend on the relative distribution and domain sizes of the tetragonal inclusions. We demonstrate,

that efficient transfer can lower the threshold for amplified spontaneous emission in the material from which we deduce design principles for mixed phase architectures to tackle the problem of Auger recombination and to suggest materials for lasing applications.

The role of crystal structure in the optical properties and excitonic many-body effects in two dimensional lead-halide perovskites

Electro-optical properties of materials are inherently linked to the symmetry and dimensionality of a material system. Excitons in two dimensional semiconductors are strongly bound and exhibit a broad variety of physical phenomena promising for quantum optoelectronics. Two dimensional layered perovskites form a subclass in the perovskite family and self-assemble in a multiple quantum well like configuration, resulting in charge confinement within the inorganic layers and high exciton binding energies. Consequently, these materials show usually the narrowband finger print of free exciton absorption and emission. Nevertheless, a small group of them feature broad photoluminescence bands, and some compounds develop a distinct excitonic fine structure at low temperatures. To shed light on the underlying mechanisms of these peculiar optical characteristics we use a combination of structural and optical probes to study three structurally different compounds, (EDBE)PbI₄, (NBT)₂PbI₄ and (PEA)₂PbI₄ showing broad and

narrow-band emission, and a pronounced excitonic fine structure respectively. We demonstrate that these optical effects are closely linked to the intrinsic crystal structure. Deformations of the inorganic cage induced by the self-organization of the organic cation within the crystal lattice result in deactivated Raman modes in the system and affect defectivity and charge localization energy, causing the broad photoluminescence features. Excitonic fine structure arises due to a reduction of crystal symmetry and we discuss possible origins like Jahn-Teller effects and Rashba-Dresselhaus mechanism. Using two dimensional coherent spectroscopy, a technique with superior spectral and time resolution with respect to regular transient absorption spectroscopy, we evidence the presence of this fine-structure even at room temperature and investigate the influence of lattice deformations and structural disorder on the excitonic many-body effects in these materials. We provide the first direct observation of stable biexcitons in (PEA)₂PbI₄ and point out the influence of lattice fluctuations and induced disorder on many-body effects, which are of paramount importance for the mechanisms of photonic or polaritonic lasing and therefore to advance hybrid perovskites towards progressive technologies.

SINGLE-PIXEL IMAGING: DEVELOPMENT AND APPLICATIONS OF ADAPTIVE METHODS

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Single-pixel imaging (SPI) is a trendy paradigm that allows the acquisition of images at reasonably low cost, and with hardware compression of the data. The architecture of a single-pixel camera (SPC) indeed consists of only two elements: a spatial light modulator, and a single-point detector. The key idea is to modulate the image that is observed with a certain pattern, and to collect the corresponding measurements at the single detector. The desired image can then be restored by post-processing the sequences of measures performed with several patterns.

Probably, the first concept of modulation of a light field and collection of the output light on a single detector was reported in 1982. Back then, it was proposed to use the piezoelectric-elasto-optic effect of crystals for modulation, such that the light output is proportional to the Fourier transform of the imaged object. However, at that time, building small and numerous crystals was not as accessible as it is today, and only a proof of concept with a few crystals was reported, without restoring an image of the object. As a result, the credit for the SPC has been

attributed to Rice University, where the first SPC images were obtained almost 25 years later. At that time, the pioneering idea of compressive sensing (CS) proposed by Donoho in 2006 opened the door for people to use the SPC with random patterns in the same year, and to reconstruct an image using l_1 -minimization algorithm. Since then, the algorithms have evolved, new acquisition strategies have been proposed, and the SPC has found many different applications.

At first glance, having a single pixel can appear to be counterproductive, as the cameras of today embed several millions of pixels. However, several advantages stand out when

compared to cameras based on an array of sensors (i.e., CCD or CMOS cameras architectures). First, single-point detectors usually have high efficiency, and can therefore detect weak light intensity changes. In medical applications, this can be very useful, as tissue absorption is usually quite high. Secondly, there is intrinsic compression at the hardware level when using a SPC, which hence needs small storage memory. This is a key advantage in applications where the data rate for transmission would be low, such as remote-imaging applications (e.g., aerospace remote sensing). Finally, a single-point sensor imaging device is usually less expensive than a sensor-array-based camera. The

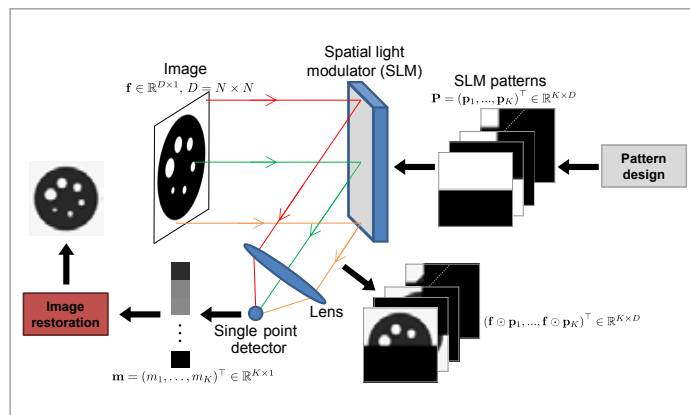


Fig. 1 - Single-pixel camera set-up with its two related problems: pattern design and image restoration based on the measurements

SPC is therefore well suited to infrared imaging, where the use of a conventional imaging system that operates at these wavelengths would be costly.

The latter advantages of SPI and the nonionizing nature of the optical imaging make the SPC an excellent candidate for biomedical imaging applications. For instance, a low-cost, time-resolved imaging system can benefit fluorescence lifetime imaging, by coupling the point detector with a photon-counting board. Adding a spectrometer further allows a complete multispectral time-resolved system to be obtained, to supplement the lifetime information of tissues with its spectral content. The SPC can also be used for imaging through scattering media, for diffuse optics (e.g., skin lesion detection or intraoperative), for ophthalmology, and to characterize tissue properties using near infrared illumination. Through exploiting several SPC images, this can provide fluorescence molecular tomography and diffuse optical tomography, with applications for molecular imaging and oximetry.

The goal of this thesis is to investigate SPI for biomedical applications. One of the main

limitations of the SPC in previous studies is the speed of acquisition and/or image restoration. In such cases, real-time applications cannot be considered, which rules out interventional imaging (e.g., fluorescence-guided surgery), for instance. Therefore, for biomedical imaging using a SPC, it is necessary to develop specific techniques for acquisition and/or restoration.

To meet the goals of this thesis, a new acquisition strategy for SPC was proposed to reduce the reconstruction times, which is referred to as adaptive basis scan by wavelet prediction (ABS-WP). This technique uses the wavelet transform for two-dimensional (2D) images with an acquisition strategy based on fast interpolations and multiresolution approximations. Simulated and experimental data show the efficiency of ABS-WP, compared to some of the other SPC acquisition techniques such as compressive sensing. Then, a method to halve the number of measurements is proposed. This was designed because patterns with both positive and negative entries cannot be implemented on a spatial light modulator. To deal with this technique, it is common to separate the pattern into its

positive and absolute negative parts, whereby the subtraction of these two measurements provides the desired measurement. This, however, doubles acquisition times, as twice the number of measurements need to be performed. Here, the problem is formalized from a general point of view, with the demonstration that a semi nonnegative matrix factorization (SNMF) algorithm can be used to overcome the experimental constraints, and therefore to reduce the necessary number of measurements. Finally, the SPC with the techniques developed previously is used for applications that can benefit biomedical imaging. A temporal dimension is added to the SPC to perform fluorescence lifetime sensing, lifetime being an important parameter for biologists to assess the tissue micro-environment (e.g., pH). Then, a spectral dimension was further added to obtain multispectral, time-resolved measurements. The obtained SPC system coupled to our acquisition strategy ABS-WP allows complete differentiation between the different components of the imaged object using the spectral and temporal information.

ULTRAFAST ELECTRON MICROSCOPY: CHARGE DYNAMICS IN SEMICONDUCTORS AND INSULATORS

Vittorio Sala - Supervisor: Alberto Tagliaferri

The size of a system and the speed of its temporal evolution are strictly related. The Earth has a radius of 12'000 km and takes one day to complete a rotation around its axis. A butterfly is smaller than the Earth and moves its wings much faster. Nonetheless, absorption of light by materials generates phenomena billion times faster than the wings of a butterfly. Lasers generate light pulses short enough to study those phenomena. A strong pulse excites the material, while a second one allows to take a picture at a chosen delay acting as the flash of a camera. Nonetheless, the devices used in modern electronics are too small to be observed by light even using an optical microscope. The electronic microscope allows to study morphology, chemical composition and defects of the materials used in electronics. During the thesis, an Ultrafast Scanning Electron Microscope (USEM) has been developed to join the potentials of laser-based experiments and electronic microscopy. The experimental setup, shown in figure 2, has been optimized to study the effect of light on the electric charges near the surface of materials. Scientific cases that were studied are silicon, the most used semiconductor in electronic, and aluminum oxide,

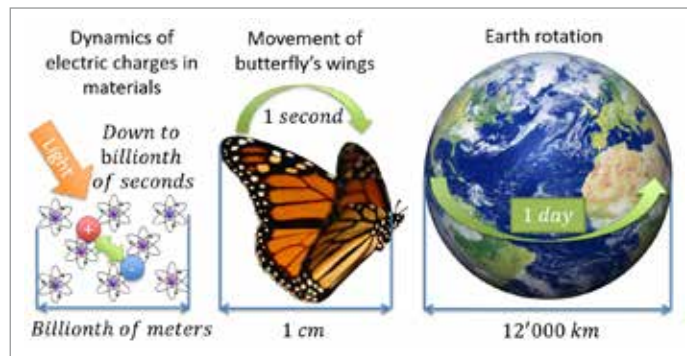


Fig. 1 - The evolution time of the system depends on its size. The earth is huge and slow, the butterfly seems small and fast, but the dynamics of electric charges in materials may be billions of time smaller and faster.

an insulator. The knowledge acquired has the goal to improve photovoltaic solar panels, that convert light into electricity. A laser generates UV light pulses that are focused on the sample. A branch of the beam reaches the ultrafast electron source, a device that converts optical pulses into electron pulses. In USEM, the electron pulses are focused on the surface of the sample. Nearby the impact point electrons of the material are excited and may be emitted. Intensity of emitted electrons is reported in grayscale images. A movable mirror allows to change the length of the light path, controlling the delay of the electron pulse with respect to the optical one on the sample. If the electron pulse arrives on silicon before the optical one, the

USEM image appears uniform, except for some grains of dust. On the opposite, if the electron pulse arrives after the optical one, a circular spot appears in the footprint of the laser. Results show that the brightness of the spot depends on the concentration and type, n or p, of dopants in silicon, that are defects introduced in semiconductor crystals to improve electrical properties. On pure and n-type silicon the spot appears bright, meaning that light enhances electron emission. The opposite happens on p-type silicon where the spot appears dark. Brightness of the spot has been studied versus the delay of the electrons with respect to the photons, as shown in Figure 3. Recovery is described by an exponential

decay with time constant of few nanoseconds, billionth of second. Proposed theoretical model is based on the hypothesis that emitted electrons are sensitive to the electric charges generated by light inside the material. Recovery of the contrast is, therefore, a measurement of the recombination of those charges, according to the Shockley-Read-Hall model. In highly n-doped silicon recovery process is ten to hundred times faster, with a time constant of few tens of picoseconds. The faster dynamic is attributed to an interaction between electric charges in the material and surface defects. The hypothesis is confirmed by test showing that exposure of the sample to oxygen affects the observed optically-induced contrast and its recovery. Further measurements were done on aluminum oxide, namely an insulator where electric charges are fixed. A bright spot was observed and attributed to color centers, defects in the crystals due to missing atoms that give the charges in the material some freedom to move. Colors centers were excited both by electrons and by photons. USEM allowed unveiling the dynamics of the contrast. The recovery of optically induced contrast, experimentally measured, is compatible with radiative decay of excited color centers, measured by time-resolved photoluminescence. Results obtained confirm that USEM is sensitive to the charge dynamics at the surface of insulators and semiconductors with a time resolution of few ps. The perspective is to study

not only the generation and recombination of electric charge in materials, but also their evolution including spatial displacement.

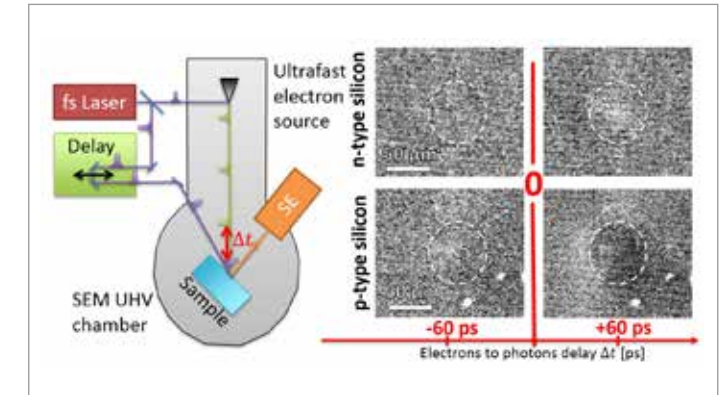


Fig. 2 - Sketch of the experimental setup of Ultrafast Scanning Electron Microscope (USEM). Laser light excitation determines a bright contrast on n-type silicon and a dark contrast on p-type.

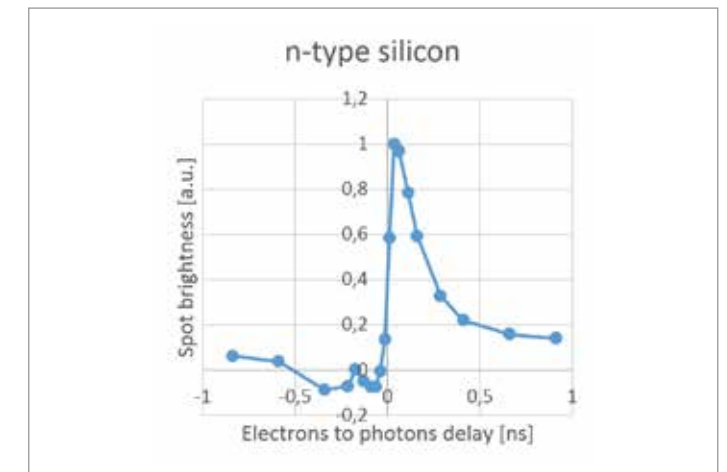


Fig. 3 - Spot brightness versus electrons to photons delay at the surface of n-type silicon

CONJUGATED POLYMER PARTICLES: A BIDIRECTIONAL STRATEGY FOR LIGHT-BIOSYSTEM INTERACTION

Elena Zucchetti - Supervisor: Maria Rosa Antognazza

Tutor: Guglielmo Lanzani

In recent years, organic semiconductors arose as a class of materials for multifunctional applications. They have been widely used for photovoltaic applications thanks to their distinctive optoelectronic properties. Interestingly, conjugated polymers possess a carbon-based structure which closely resembles the chemical structure of biological molecules expressed in retinal cells. Furthermore, their unique properties of biocompatibility together with the possibility to exploit their optoelectronic properties make conjugated polymers ideal for exogenous modulation of living cell activity. It has been previously demonstrated that thin films made by poly(3-hexylthiophene) (P3HT) can be used as photoactive layers to stimulate a light-induced response in explanted chick retinas and to realize the first *in vivo* and long term implantable retinal prosthesis device. Giving the outstanding potential of these materials, investigation on different nanoscaled architectures has been gaining considerable attention. The aim of this thesis dwells on a detailed study of the interaction between P3HT nanoparticles (P3HT-NPs) and living cell cultures, both from a

physiological and photophysical perspective. P3HT-NPs fabrication consists in the application of the straightforward reprecipitation method for obtaining surfactant-free suspensions with excellent colloidal stability. Through this process, it is possible to obtain NPs under sterile conditions with highly reproducible morphological properties, which are essential for biological applications. Morphological, physical and optoelectronic properties of NPs are characterized by a combination of different experimental techniques. Hydrodynamic diameter values and polydispersity indexes are obtained by Dynamic Light Scattering (DLS), while UV-VIS and fluorescence spectroscopy are used to confirm the preservation of optical properties of the pristine polymer. Figure 1a shows a representative image acquired by Scanning Electron Microscopy (SEM), highlighting the well-defined spherical shape and smoothness of surface particles. Cytotoxicity of P3HT-NPs is an issue of great relevance for *in vitro* and especially *in vivo* applications. Therefore, P3HT-NPs synthesis is carried out under sterile conditions, and biocompatible assays are performed. P3HT-NPs

are incubated with Human Embryonic Kidney (HEK-293) cell cultures. A colorimetric assay, that assesses cell metabolic activity, demonstrates that cell proliferation after NPs incubation is not compromised. Along with this information, it is necessary to establish whether P3HT-NPs undergo internalization during cell incubation. Combined analysis of fluorescent stained cell cultures (Figure 1b) and confocal imaging provides evidence about the localization of P3HT-NPs within the cell cytoplasm but outside the nuclear membrane. The effect of P3HT-NPs on cell functionality is then evaluated. Calcium Ca^{2+} ions are at the basis of intracellular signals, and pathological conditions of cell workings can be identified by observing dynamics of intracellular calcium fluxes. No permanent alterations of the physiological cell activity are evidenced. Polymer NPs uptake may also impact on cell membrane electrical properties, such as resting membrane potential, capacitance and resistance. Their possible impact has been evaluated by electrophysiology experiments in voltage clamp configuration. Samples treated with P3HT-NPs do not show any statistical differences with control samples, meaning

that NPs internalization do not affect lipid membrane properties persistently. P3HT photoluminescence has been largely studied for photovoltaic applications. In our case, it is important to investigate P3HT-NPs photophysical properties before and after plasma membrane crossing, in order to highlight a possible role of plasma proteins. Time-resolved photoluminescence (TR-PL) uncovers peculiar features of NPs emission, in particular a low-energy PL shoulder that is no more visible in spectra of NPs internalized within the cell cytosol. We possibly ascribe this behaviour to the presence of loosely bound chains protruding from the surface of the NPs and interacting with the intracellular environment. The absence of cytotoxic and physiological effects on cell workings together with the peculiar behaviour of PL properties make P3HT-NPs a suitable candidate for use as biological probes.

Besides that, in this thesis we are mainly interested in exploring new technologies for light-biomatter interaction, in particular we want to demonstrate the feasibility in inducing a cell bioelectrical response upon illumination. The particle surface is the region that especially interacts with the environment. A new route can be explored by tailoring the active polymer with functional groups, like N-succinimidyl-ester (NHS) group, to selectively bind NPs to amine groups on membrane proteins. Thus, NHS-NPs were incubated with HEK-293 cells, and confocal microscopy confirmed NPs docking on cell membranes even after 24 hours of incubation. By applying whole-cell current clamp under light illumination, we could successfully induce a significant change in cell membrane potential as well (Figure 1c). We conjecture that the light-induced polarization of cell membrane can have a thermal origin combined with the effect due to the intimate contact

between the material and the lipid membrane, even if other electrical or chemical effects cannot be excluded. Finally, a new perspective over possible implementations of polymer NPs structure is given, towards the realization of a new platform of organic nano-actuators capable to interact with living systems by means of light.

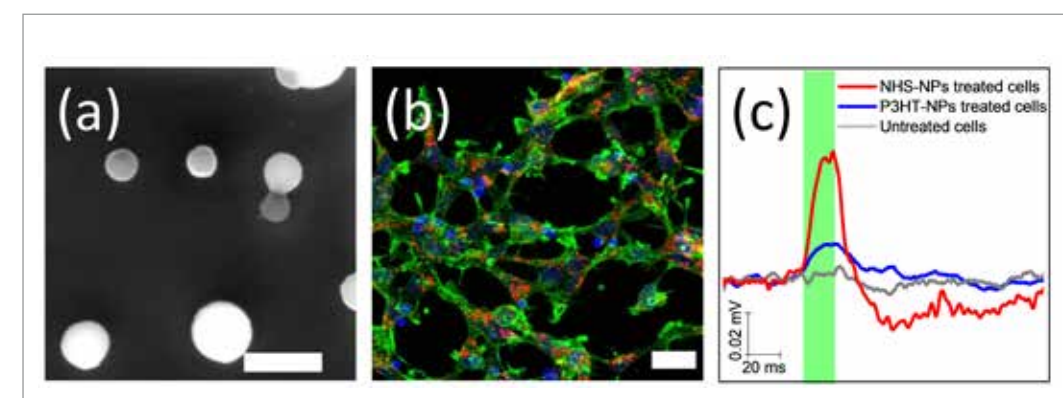


Fig. 1 - (a) Representative SEM image of P3HT-NPs. Scale bar, 500 nm. (b) Fluorescent imaging of HEK-293 cells incubated with P3HT-NPs (red emission) and stained with DAPI (cell nuclei, blue emission) and Phalloidin (cell cytoskeleton, green emission). Scale bar, 30 μ m. (c) Representative membrane potentials variation traces for cell cultures treated with NHS-NPs (in red), P3HT-NPs (in blue) and control samples (in grey), and illuminated for 20 ms.