





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.

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

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

Family Name	First Name	Position*
Ghiringhelli	Giacomo	Ap
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	Ap

Family Name	First Name	Institution
Pirovano	Agostino	Micron Semiconductor Italia s.r.l.
Donati	Fabio	EPFL – Lausanne, CH
Hecht	Bert	Universität di Würzburg, D
Luridiana	Sebastiano	Tecno Vacuum s.r.l.
Blandino	Davide	Optec s.p.a.
Majorana	Salvatore	IIT – Technology Transfer Office

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.

The average number of fellowships available for students admitted to the PhD Program is fifteen per year. At present, the number of students in the three-year course is fifty-eight, and forty-seven 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.

# VOLTAGE CONTROL OF MAGNETIC ANISOTROPY IN METAL-OXIDE HETEROSTRUCTURES

**Baldrati Lorenzo – Supervisor: Prof. Riccardo Bertacco**

A diverse ensemble of properties of metal-oxide interfaces is determined by the interaction between the oxide and the metal, such as the chemical, electronic, mechanical and magnetic ones. Since the behavior of nanoscale devices largely depends on the interface properties, the possibility to control them by an electric field is both promising from the technological point of view and interesting from the theoretical one. In particular, the possibility to switch the magnetization by an electric field may allow to sizably reducing the amount of power dissipated during writing of Magnetic Random Access Memories (MRAMs). The advantage of this approach lies in the fact that, instead of switching the magnetization by a highly-dissipating current, as done in the state-of-art MRAM technology, the switching of the magnetization may be obtained by a low-dissipating electric field applied across an insulator, requiring only the energetic cost of charging of a capacitor. In addition to this potential improvement of the existing technology, the control of the magnetic properties by a voltage may lead to the creation of new kinds of solid state devices, e.g. for the processing of magnonic signals by the creation

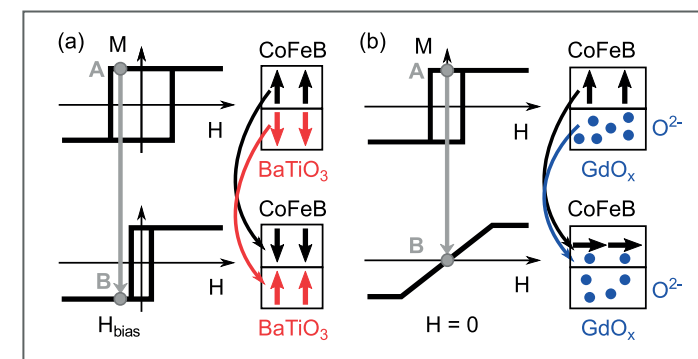
of reconfigurable patterns and landscapes in magnetic materials. In this thesis, two possible routes toward electric control of magnetic anisotropy will be discussed, namely the composition of artificial multiferroics (CoFeB/BaTiO<sub>3</sub>) and the use of magneto-ionic systems (CoFeB/GdOx). Artificial multiferroics are systems where a ferromagnetic and a ferroelectric material are coupled at an interface, so that it is possible to control the properties of the ferromagnet by changing the polarization of the ferroelectric material, leading to the converse Magneto-Electric Effect (MEE). In this thesis, we report on the CoFeB/BaTiO<sub>3</sub> heterostructure (see also Adv. El. Mat., 2, 7, 1600085, 2016). In this system, the magnetic coercive field of an ultrathin CoFeB layer can be controlled by the ferroelectric polarization of a barium titanate thick film (BTO) by a relative amount of 60%. Even if the effect of the strain cannot be completely excluded, we believe that the main contribution stems from the charge induced at the interface of the ultra-thin CoFeB layer by the electric dipole moments of the barium titanate. This modulation of the magnetic coercive field can be used to switch the

magnetization electrically, since a stable magnetization state when the coercive field is high, becomes unstable if the coercive field is reduced by the effect of the ferroelectric polarization, in presence of an external magnetic bias field (see Figure 1a). This electrically assisted switching can be performed for positive as well as negative magnetic bias fields and it is non-volatile. A magnetic field applied on a large area may be used in combination to a voltage to switch only selected devices in a memory chip. However, we found that the switching dynamics is dominated by magnetic viscosity. A 4000% modulation of the switching time is seen as a function of the BTO ferroelectric polarization. This ratio represents a figure of merit of the device, since it is the ratio between the retention time of a “stable” state, respect to the switching time of the “unstable” one, whose switching is desired. The magnetic bias field has to be chosen as a compromise between a fast switching time and a long stability time. In order to avoid the need of an external magnetic bias field, a system presenting a spin reorientation transition, i.e. the change of the magnetic anisotropy axis from perpendicular-to-plane to in-

plane, is needed. This is possible by means of the magneto-ionic effect, which is the possibility to control the magnetic properties of a ferromagnetic metallic layer, by a voltage-driven oxidation. O<sup>2-</sup> ions can be moved by an electric field in a solid-state ionic conductor, and they can modify the anisotropy of a nearby ferromagnetic layer via the oxidation of the latter. This effect was recently demonstrated in Co/GdOx. Here we show that the magneto ionic effect can be achieved also in CoFeB/GdOx. The use of CoFeB is motivated by its technological importance, since it is used as a ferromagnetic electrode in CoFeB/MgO/CoFeB MRAMs. The magnetic properties of CoFeB in the CoFeB/GdOx system depend on the voltage applied across GdOx, via the magneto-ionic effect. We have detected this effect both in Ta/CoFeB with In-plane Magnetic Anisotropy (IMA) and in Pt/CoFeB with Perpendicular-to-plane Magnetic Anisotropy (PMA). In particular, the perpendicular magnetic anisotropy is strengthened when the oxygen ions migrate into the CoFeB layer, while it is weakened when the oxygen ions are driven out of the CoFeB layer. A spin reorientation transition was obtained in Pt/CoFeB at ±2V, by which we set a lower limit for the interface magnetic energy anisotropy variation of 0.2 mJ m<sup>-2</sup>. We also observed an electrical modulation of the CoFeB magnetic properties

in CoFeB/Ta, but in this case no spin reorientation transition is seen, while the slope measured by MOKE changes for applied voltages of ±10 V. The existence of a spin reorientation transition based on the magneto-ionic effect is interesting in view of future applications. In order to test the feasibility of such an approach and with the aim of demonstrating the switching of a free layer by the magneto-ionic effect in a device, we fabricated Co/GdOx/Co Magnetic Tunnel Junctions (MTJs), which act as linear magnetic field sensors. GdOx is a good tunneling barrier at room temperature, in good agreement with the Brinkman model of tunneling.

As-fabricated Co/GdOx/Co MTJs present a sizable Tunneling Magneto-Resistance (TMR) of 1.9% at 300 K, which is not enough for application in MRAMs. Interestingly, resistive switching was observed in these junctions at a voltage similar to the ones leading to the magneto-ionic effect, but the TMR in the Low-resistance state (LRS) is decreased to less than 0.2%, which does not allow to probe the magnetic state of the electrode. An annealing in vacuum in presence of an applied magnetic field improves the TMR ratio, which may allow the detection of the TMR in the LRS. This will be addressed in future studies, as well as the assessment of the potential of the magneto-ionic effect in devices.



**1. (a) Scheme of the electrically assisted magnetic switching in CoFeB/BaTiO<sub>3</sub>. The coercive field of the CoFeB can be controlled by the interaction between the electric dipole moment in the ferroelectric BaTiO<sub>3</sub> and the magnetic moments in the CoFeB. If the system is prepared in state A and the ferroelectricity of the BTO is flipped, state A is not stable anymore and the system goes to state B. (b) Scheme of the spin reorientation transition in CoFeB/GdOx, induced by the motion of the oxygen ions (depicted by blue circles). Remarkably, this transition can occur in absence of an applied magnetic bias field.**

## MULTI-ANALYTICAL APPROACH FOR THE STUDY OF MODERN SEMICONDUCTOR PIGMENTS

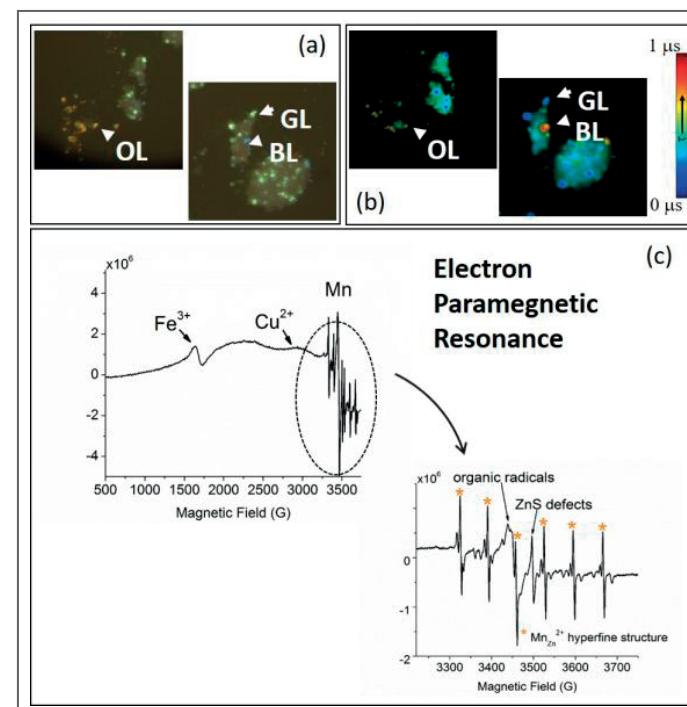
Bellei Sara – Supervisor: Dr. Austin Nevin

The use of physical methods for the investigation of art's materials has undergone a steep increase over the past years. The application of existing analytical procedures to heritage materials contribute in the understanding of their physical and chemical properties and helps in defining efficient protocols of intervention on works of arts and art's materials, in situ or in laboratory, preferably in a non-invasive manner.

UV, VIS, or IR light is commonly employed by conservator for the inspection of works of art to reveal important features such as the presence of imperfections and evidence of restoration, and to select sampling locations for further analysis. Advanced spectroscopy techniques provide a chemical and physical description of cultural heritage materials with a non/ or micro-invasive approach. The range of materials that can be studied with this approach is very broad and encompasses painting materials, ceramics, and metals. Modern inorganic pigments highly benefit of a multi-analytical approach which includes optical spectroscopy and imaging. Modern pigments such as zinc whites, cadmium yellow and red, prussian and cobalt blue, have been introduced into the

market following the industrial revolution, and the subsequent flourishing of chemical industries. The properties of these pigments depends to a greater extent on the manufacturing process; their degradation processes constitute a challenging problem of present conservation science. This thesis reports results of the application of a multi-analytical protocol of investigation for the understanding of optical properties of historical semiconductor pigments. The analysis protocol included spectrally- and lifetime-resolved photoluminescence (PL) techniques, and Electron Paramagnetic Resonance (EPR) spectroscopy. Lithopone white is a modern semiconductor pigment which consists of a co-precipitation of zinc sulfide and barium sulphate ( $\text{ZnS}+\text{BaSO}_4$ ). It was first manufactured on commercial scale in 1874. Its usage as an artists' pigment remains nowadays difficult to establish, and little studies have been dedicated to it before. Optical properties of lithopone strongly depend on the ones of ZnS. ZnS is a semiconductor of the II-VI group with a large, direct band gap of 3.54 eV (cubic form) at room temperature. When is doped with suitable activator,

such as transition metals, ZnS extends its range of emission up to the infrared spectrum, with recombination occurring via trap states. Historical lithopone often shows a strong green luminescence characterized by a long-living emission lifetime. This feature motivated to further investigate optical properties of lithopone pigments. First, historical synthesis processes of lithopone were studied. ZnS was obtained by chemical process of its primary ore Sphalerite. In Sphalerite, fluorescence usually occurs when specific impurities are present within the mineral. Under the hypothesis that historical lithopones were produced using non perfect synthesis processes, it can be considered that these impurities were not completely eliminated during the manufacturing of the pigment, acting therefore as luminescent centers. *Figure 1.a* shows the RGB reconstructed image of the fluorescence at a microscale of a selected sample. Small, localized luminescent centers of variable color, diameter, and intensity were observed. In *Figure 1.b* time-resolved PL imaging of the same areas is showed. The microsecond decay-kinetic behavior of the emission confirmed the trap state nature of the luminescence



**1. (a) Reconstructed RGB images of the UV-induced PL emission for a selected historical lithopone sample under microscope magnification. (b) Lifetime maps of the same areas following monoexponential decay data fitting from 0 to 1 ms, shown in false color. (c) EPR spectra. The  $\text{Fe}^{3+}$  signal were attributed to Fe impurities, often present in sphalerite.  $\text{Mn}^{2+}$  and  $\text{Cu}^{2+}$  ions in ZnS matrix were also observed.**

centers, reinforcing the hypothesis that luminescence in historical lithopone is due to metal ions impurities embedded into the crystal lattice. EPR (*Figure 1.c*) confirmed the presence of  $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$  into ZnS matrix which could not be detected by common elemental analysis such

as bulk X-ray Fluorescence. A similar protocol of investigation was applied to the study of a set of historical cadmium yellow pigments. Cadmium yellows are modern yellow colors composed of cadmium sulfide ( $\text{CdS}$ ) or cadmium-zinc sulfide ( $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ ). A gradual fading of

cadmium yellow from exposure to light and atmospheric agents have been observed on several painting; chemical degradation paths of cadmium colors have been therefore widely studied in the past years. Nevertheless, few studies related with optical properties of historical cadmium pigments. The samples under investigation showed an unexpected heterogeneity of the PL emission when observed under the microscope. Different hypotheses were proposed for the explanation of the observed results. In future, the complex composition of historical cadmium pigments should be taken into account for the understanding of their degradation paths. The multi-analytical approach presented in this thesis for the study of optical properties of semiconductor pigments encourage further exploration of the same protocol for the study of the intrinsic heterogeneity of other painting materials.

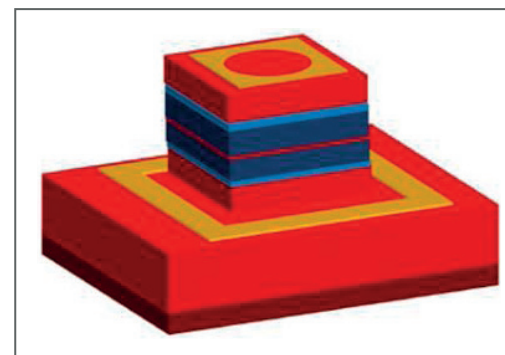
# DROPLET EPITAXY QUANTUM DOTS FOR INFRARED DETECTION APPLICATION

Esposito Luca – Supervisor: Prof. Giovanni Isella

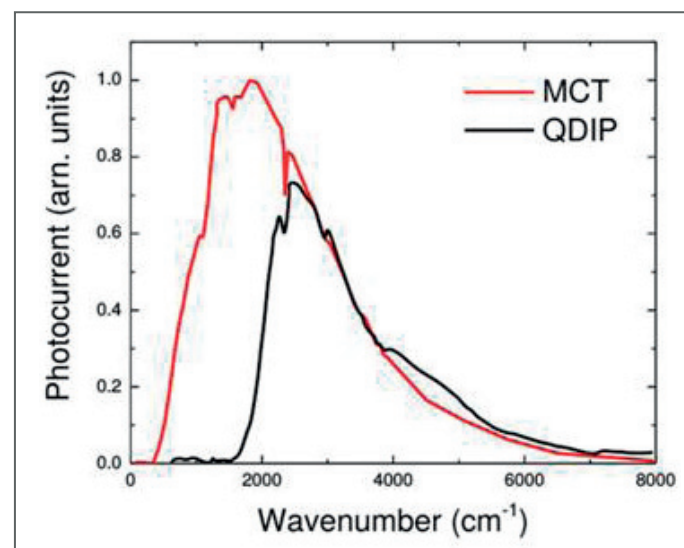
During the 20th century military applications in western countries (e.g. navigation, weapons detection, night vision) have spearheaded and dominated the requirement of infrared (IR) detectors. Nowadays, the market of IR technology has become wider and the applications currently utilizing IR detectors span commercial (e.g. communications, aerospace, medical imaging), public (e.g. atmospheric sounding, pollution control, meteorology, environmental monitoring), and academic (e.g. astronomy) domains, with new uses constantly arising as the various IR technologies become more established (e.g. automotive, smart-phone, building automation). Future employments and applications of IR sensors for imaging purposes are closely linked to the possibility of the development of a new generation of sensor: the “third generation”. The “third generation” of photo-detectors will provide enhanced capabilities such as larger number of pixels, higher frame rates, better thermal resolution and in particular multi-spectral functionality. In the IR regions of interest such as SWIR, MWIR and LWIR, four major technologies are developing multi-spectral capability: the HgCdTe photo-detector, the quantum well

infrared photodetector (QWIP), the quantum dot infrared photodetectors (QDIP) and some antimonide based type II superlattices. In this PhD thesis in particular we have analysed the possibility of developing 1) a QDIP based on a quite new strain-free techniques called “droplet epitaxy” and 2) we have explored the possibility of monolithically integrating this device on silicon-germanium substrates employing different strategies developed in the L-ness laboratories in Como. In the first chapter of the thesis a brief but quite complete introduction on the IR radiation, IR sensors and their market, their classification, architecture and functioning has been given. In the second chapter of the thesis the relationship between QDIP and QWIP are analyzed stressing on the advantages given by the 3D confinement. In particular the inhibition of incident absorption for the QWIP and the possibility of overcoming this issue with the QDIP is looked through the analysis of the quantum mechanical selection rules coming from the envelope function formalism. Furthermore, during this chapter, some state of the art QDIP design is presented and some of their feature is discussed. In the third chapter of the thesis an

introduction to the used molecular beam epitaxy (MBE) system and in particular to “droplet epitaxy” techniques has been given. Major emphasis has been dedicated to the explanation of the versatility of a strain-free growth such as droplet epitaxy, especially for what concern the human capability of fine tailoring quantum properties and energy levels in nanostructures, and in particular in QDs. In the fourth chapter the interest and the issues related to monolithic integration of III/V materials on Si are briefly discussed. Three strategies developed in our laboratories are described as possible solutions. Two of these strategies are going to employ (111) orientated substrates. However in scientific literature the growth of GaAs (111) is far to be optimized especially for what concern the (111)A orientation. For that reason in the central part of this chapter we have presented the morphological study we made and the model we have constructed to understand the prominent growth mechanisms that could lead to the growth to an highly flat surface ( $RMS < 0.2$  nm) and so to a right field for a fine tuned of nanostructures on this surface. At the end of the chapter a macro photoluminescence (PL) spectra of



1. Sketch of the finished device



1. FTIR measurement of QDIP absorption compared (on another scale) with an MCT detector

a 5.5 nm thick QW is presented. The spectra shows a very narrow broadening of 4.2 meV, demonstrating the high flatness achieved. The last chapter is the one dedicated to the QDIP manufacturing. In the first section a detailed description of the growth and of the design is given. In the second section all the processing procedures are described with particular stress on the MESA etching and metal deposition.

These two steps have been particularly demanding for what concern the developing of the recipe of the wet etching solution and the right choice of the metallic alloy for the fabrication of ohmic contacts. In the third section the electrical characterisation of the device is presented. Starting from the description of the method to evaluate the quality of our contacts we have measured the contact resistivity and so their “ohmicity”. The proper

characterization of the device has been conducted starting from the measurement of the dark current values under a bias range of  $-2V < \text{bias} < 2V$  at room temperature. Different generations of samples with different intrinsic layer thickness have been characterized, looking at the dependence of dominant dark transport regime on the thickness. The temperature characterization has been conducted in a closed-loop He cryostat, on which a field-assisted transport is recognized as prominent effect on the dark current generation just over the  $|0.7|$  V, while under thermionic regime is identified as prominent one. The verification of the IR absorption in the expected region (4  $\mu\text{m}$ ) is conducted in two phases. In the first phase the absorption is verified in a setup for cryogenic photocurrent measurement, in the second phase the spectral shape of the photocurrent is measured by the mean of a Fourier transform infrared spectrometer in collaboration with Patrick Rauter of the Johannes Kepler University of Linz. A qualitative comparison (different scales) with a commercial HgCdTe (MCT) detector reveals that the region of detection is the right one and the signal to noise ratio is strongly improved respected to the first generation of QDIP.



# ATTOSECOND MULTI-ELECTRON DYNAMICS PROBED BY HIGH-ORDER HARMONIC GENERATION IN TWO-COLOR FIELDS

Faccialà Davide – Supervisor: Prof. Salvatore Stagira

Attosecond science aims at measuring electronic dynamics and correlations in atoms, molecules and solids in their natural time-scale. This new frontier of science promises to get new insights in a wide range of research areas, from atomic and molecular physics to chemistry, medicine and biology. It is this background that makes it compelling for scientists to overcome the actual frontiers of attosecond spectroscopy, designing and developing new techniques for probing electronic motions on the attosecond time scale.

Recent developments of ultrashort and intense tabletop laser sources have enabled to probe matter in a strong non-linear regime, allowing to trigger, control and measure the electronic structure and dynamics occurring. Among the available processes initiated by strong field laser-matter interaction, one of particular interest is high-order harmonic generation (HHG). In a single active electron (SAE) picture, during this process the laser field tunnel ionizes an electron from the valence state, it accelerates this electron up to high kinetic energies, driving it back to the parent ion where it recombines, emitting radiation. The HHG spectrum usually shows

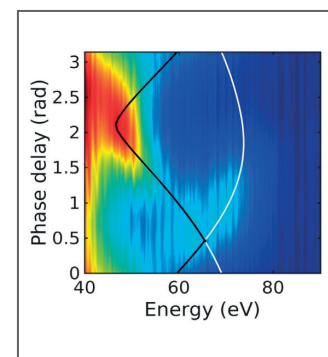
a plateau, where two possible electron trajectories interfere, that extends up to a cutoff energy, beyond which the intensity exponentially decreases and only one possible cutoff trajectory is allowed. This trajectory has no classical analogous, but its presence is due to the quantum nature of the process. HHG emission encodes the electronic structure of the target and the dynamics involved during the process. However, it encodes also a complexity of other phenomena, such as interference of different trajectories, which must be aptly disentangled from the measurement in order to have access to the quantities of interest. In order to do so, we can add one dimensionality to the output by generating high-order harmonics in two-color fields and acquiring several HHG spectra at different phase delays  $\phi$  between the two fields. The ability to tailor and manipulate the HHG emission constitutes the main building block of HHG pump-probe spectroscopy. The work presented in this thesis is devoted to the study of multi-electron dynamics in atoms by generating HHG from two color fields made by one field  $E_1$  of wavelength 1500 nm, and a weaker second harmonic  $E_2$ . In particular, we studied the giant

resonance in xenon, which is a broad resonance of HHG yield starting at about 60 eV and having the peak around 100 eV. The resonance has been attributed to the collective inelastic scattering of the recombining electron with the inner lying electrons in the 4d orbital just before it recombines with the valence shell.

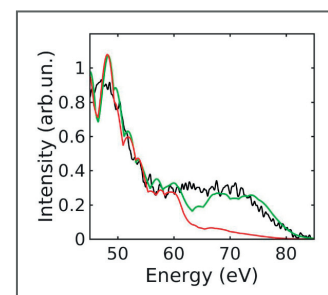
In a first experiment, the two colors have the same polarization.

**Figure 1** shows the measured HHG spectra as a function of  $\phi$ . It can be observed that the addition of  $E_2$  produces two cutoffs that change with  $\phi$  (white and black lines). The yield at the cutoff is shown in **figure 2**. We observe that the experimental yield (black line) at the upper cutoff is enhanced with respect to SAE predictions (red line). If we include the correlations with the 4d orbital (green line), we can reproduce the experimental result. In particular, the agreement at the cutoffs is also good from a quantitative point of view. In fact, at the cutoff, the solution is singular, and this offers a reliable and clean probe for making quantitative measurements of the target structure and dynamical resonances.

In the second experiment, the two colors have the same polarization. **Figure 3** shows the measured

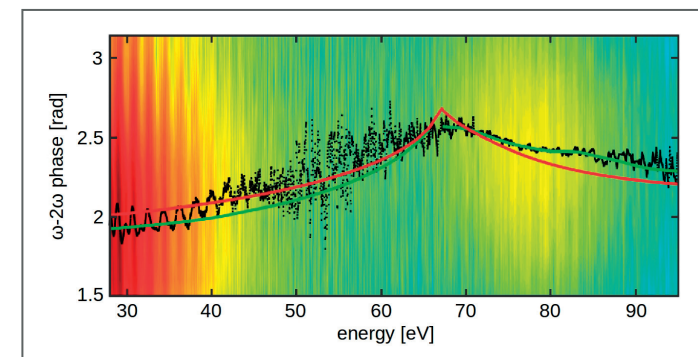


**1. HHG spectra as a function of  $\phi$ . Black and white lines represent respectively the lower and upper cutoffs.**



**2. HHG yield at the cutoffs. Black line: experimental yield. Red line: SAE yield. Green line: theoretical yield when correlations are allowed.**

spectra as a function of  $\phi$ . In this case, the tunnel-ionized electron is displaced by  $E_2$ , and recombines with the ion only at one phase  $\phi_m$  (black line). The strong change of the slope of  $\phi_m$  at 68 eV



**3. HHG spectra as a function of  $\phi$ . Black line: experimental  $\phi_m$ . Red line: SAE  $\phi_m$ . Green line: theoretical  $\phi_m$  when correlations are taken into account.**

indicates that beyond this value we are observing contributions beyond the cutoff energy. This alone is an interesting result. It tells us that the giant resonance enhances the contributions of trajectories that have no classical analogous, allowing to directly access the quantum nature of the process. The SAE calculations, that approximate the electron as a plane wave, reproduce this slope change (red line). We also observed another change of the slope of  $\phi_m$  at 72 eV that is not explained by SAE theory. By including the effect of the correlation on the free electron state, we were able to reproduce this shift, demonstrating the sensitiveness of this technique to the multi-electron process. In particular, the shift is enhanced by the fact the beyond the cutoff the

plane wave approximation fails. In conclusion, this work shows that HHG spectroscopy in tailored fields offers great opportunities for detecting and measuring multi-electron dynamics. In particular, resonant dynamics can allow the detection of cutoff trajectories, which constitute a reliable and clean probe. The quantum nature of these trajectories led to unexpected and promising results.

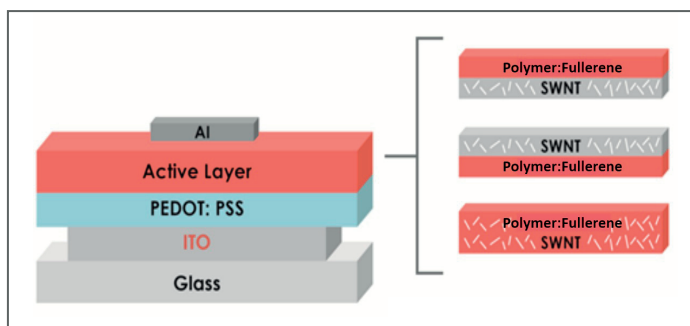
# TRANSIENT SPECTROSCOPY OF CARBON NANOTUBE/CONJUGATED POLYMER SYSTEMS

Figueroa del Valle Diana Gisell – Supervisor: Dr. Francesco Scotognella

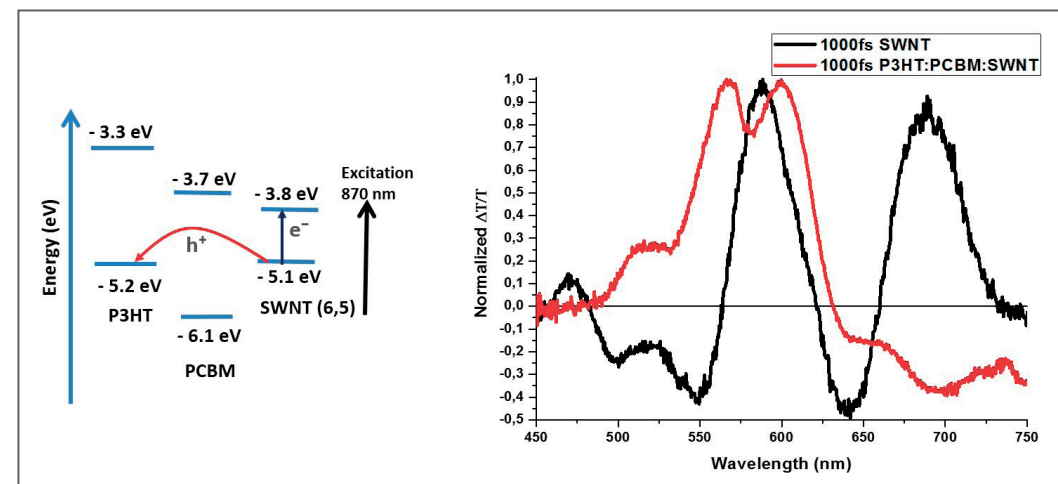
In a constant effort to reduce carbon emissions and improve friendly energy productions, renewable energies have been vastly studied during the past decades. Among then, solar energy seems to be a promising way to help to achieve the desired goals. One of the emerging research fields inside solar technologies has been organic solar cells, which within the last years have manage to arrive up to 10 % of power conversion efficiencies values. This approach is mainly envisaged to play a decisive role for indoor, building integrated and wearable applications, in which others, maybe more efficient technologies, as silicon or thin film technologies have failed to addressed. To improve the performance of this polymer based solar cells, a vast research on clarifying the key feature leading the charge generation process, that straight influences the device efficiency has been done within the last years. Among these efforts carbon nanotubes has arisen as possible building blocks to increase devices efficiencies. Many of their unique physical and chemical properties, such as chemical stability or high surface area, make carbon nanotubes a gifted material for different technological

applications. The versatility of this material has been proved in a wide range of applications going from sensors, supercapacitors, transistors to solar cells. In specific for organic solar cells, carbon nanotubes are an ideal material to improve the charge separation and/or transport of the polymer-fullerene derivatives blends used as photoactive layer in these devices. However, the past years' efforts, the charge transfer and dynamics mechanism at the interface establish between polymer:fullerene and single wall carbon nanotubes (SWNTs) is not completely understood. On the other hand, carbon nanotubes suffer from a heterogeneous source material that frequently involves a variety of different nanotube species with diverse metallicity and diameter. To get rid of these drawbacks a further selective sorting of the carbon

nanotubes, usually consuming high amounts of resources and lab time, needs to be done. In this work, the effect of the incorporation of commercially available, semiconducting (6,5) SWNTs into polymer:fullerene blends, commonly employed as photoactive layers for organic solar cells, was studied. Ultrafast transient absorption spectroscopy was employed as the main tool to study the ultrafast photophysical processes at the interface of the three different used materials. The study was conducted by selecting different (6,5) SWNTs dispersions in various dispersing solvents. Three different configurations giving rise to various interfacing scenarios were studied. The nanotubes were deposited: i) before or after the active layer as films, or ii) mixed with the polymer:fullerene blend in



1. Composition of the three different configurations studied.



2. Proposed charge transfer mechanism and band alignment for the materials present in the P3HT:PCBM:SWNT sample and Normalized transient absorption spectra at different time delays of P3HT:PCBM:SWNT (red line) and bare SWNT (black line) pump at 870 nm and probe in the VIS region, respectively.

a bulk configuration. For the studies, mainly two different efficient polymers were used, P3HT and PTB7. Interesting and diverse results, that highlight the potential of semiconducting SWNTs to improve the performance of organic solar cells, were found from the ultrafast transient spectroscopic research for each polymer:fullerene:SWNT blend. In this case, strong evidences of a direct hole transfer from photo excited SWNTs to the P3HT was found. It was also discovered that the transfer efficiency was dependent on the interface configuration and that it was increased in the case when

the blend achieved closer contact among the (6,5) SWNTs/polymer interface. The work was also extended to the fabrication of organic solar cells both in inverted and conventional geometries employing the same here different configurations as for the spectroscopy studies. From these devices was also evident the possibilities of obtain enhanced devices performances upon incorporation of SWNTs for some of the structures used. Finally, the possibility of employed the nanotubes configurations previously studied and carbon nanotube dispersions with

high excess of polymer, as semiconducting layers with improved injection behavior for field effect transistor was explored. It was observed that incorporation of SWNTs could be an easy way to enhanced the performance for polymer transistors.

# BROADBAND TIME-DOMAIN DIFFUSE OPTICS FOR CLINICAL DIAGNOSTICS, AND DIFFUSE RAMAN SPECTROSCOPY

Konugolu Venkata Sekar Sanathana – Supervisor: Prof. Antonio Pifferi

The mystery of light-tissue interaction explored by the scientific evolution can be classified into few set of basic phenomena like absorption of photons, Raman effects, fluorescence effect, stimulated emission, two photon absorption, etc. These inventions played significant role in enhancing the specificity of molecular detection, thereby revolutionized the field of *in vitro* tissue diagnostics and microscopy. However, the understanding of scattering in tissues is still at its evolutionary stage where steadfast attempts have been made by the scientific community to demystify the secrets of light propagation in diffusive media like human tissues. In recent decade, diffuse optics has been successfully advancing the studies on light-tissue interaction in diffusive media.

This PhD thesis stands at this juncture of scientific revolution, contributing to the invention and revelation of advance techniques to understand the interaction and propagation of photons in diffusive media. Thus, propelling the next-gen non-invasive diagnosis of biological tissues. The research leading to this PhD dissertation has been carried out in the physics department of Politecnico di Milano (Milan,

Italy), and two secondments at The Institute of Photonic Sciences (ICFO) in collaboration with institute and hospitals (Barcelona, Spain), PicoQuant (Berlin, Germany).

The essence of the thesis can be broken into two parts:

- 1) Time-domain Diffuse Optical Spectroscopy (TD-DOS) for Clinical Diagnostics
- 2) Diffuse Raman Spectroscopy

The key achievements of thesis are summarized below: Though diffuse optical studies are possible by continuous wave (CW) or modulated light sources. Time-domain diffuse optics is an advanced tool among them, as it can naturally disentangle absorption from scattering, provides high spatial and depth resolution. The entire DOS part of the thesis was carried out with time-domain techniques.

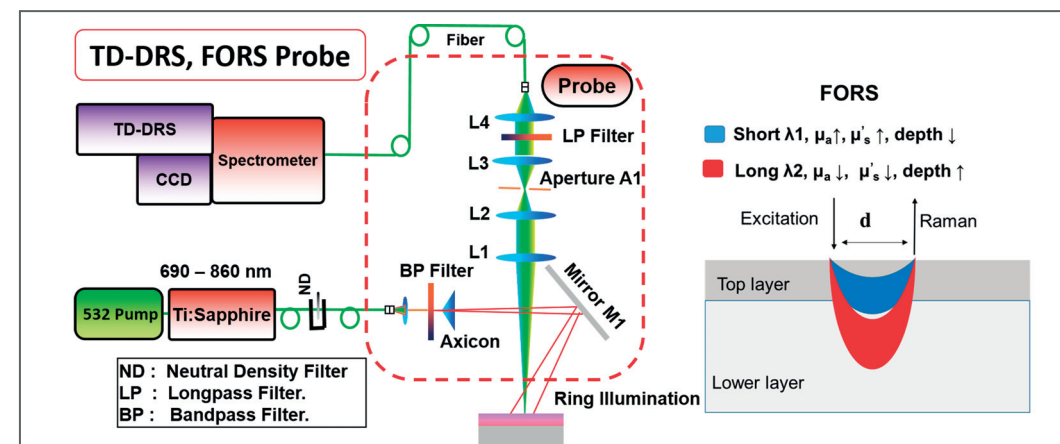
## Development of broadband (500-1350 nm) TD-DOS spectrometer

Typically, broadband TD-DOS on human tissues are carried out over 600-1000 nm. Though the tissue spectrum has interesting features beyond 1100 nm, the absence of broadband detector coupled with stringent requirements of time-domain optics and theoretical model has challenged the spectral extension. During this thesis, a

successful extension was achieved by adapting key strategies on source and detection chain optics, fibers, responsivity extension with two detector, drift and distortion compensation by IRF acquisition. Additionally, this system was designed and validated in the view of clinical application, thus making it a unique masterpiece in the world of TD-DOS.

## Discovery and characterization of new tissue constituents

Four tissue constituents namely: collagen, elastin, tyrosine, thyroglobulin were characterized during this thesis period. Importantly, high scattering, fluorescence, boundary effect and bandwidth effects are the problems tackled by means of customized probes, Monte Carlo models, bandwidth simulations, fluorescence filters, to extract absorption spectra. Characterized collagen and elastin spectra (500-1700 nm) can open key to new exploration in the beyond range (>1100 nm); breast tissue diagnosis, elasticity assessment are few potential areas of application. Tyrosine and Thyroglobulin are tissue constituents specific to thyroid organ, and this work has direct impact on non-invasive diagnosis of thyroid pathologies.



## Broadband *in vivo* studies on: Human bone, Thyroid, Manubrium, Abdomen

The broadband clinical system developed during this thesis was employed in multiple hospitals. A well deliberated protocol was carried out to measure non-invasively the above-mentioned locations. The presence of collagen in bone tissue revealed by our studies emphasized its relevance to the global diagnosis of bone pathologies like osteoporosis. The high absorption of thyroid organ led us to the discovery of new tissue constituents (thyroglobulin, tyrosine) that were absent in our data analysis, thus unlocked the new methods in thyroid diagnosis. The preliminary results of the abdomen studies for fat distinction, revealed its potential to distinguish multi-layered structure of abdomen tissues.

## Invention of Frequency Offset Raman Spectroscopy for deep tissue Raman Spectroscopy

Raman spectroscopy of diffusive media has been explored in the recent decade to extract

Raman spectrum of deep tissues. The method based on multi-distance approach, Spatial Offset Raman Spectroscopy (SORS) has revolutioned the CW diffuse Raman spectroscopy. In this dissertation, an alternative technique, Frequency Offset Raman Spectroscopy (FORS) to probe deep into tissue was proposed and demonstrated on tissue mimicking solid phantoms. The proposed technique is performed at multiple excitation wavelengths, utilizes optical properties (absorption, scattering) variations to probe deep into tissues. The figure depicts the Raman probe and the principle of FORS. FORS has been found to have superior spatial resolution and low signal to noise ratio as compared to SORS thereby making it as a valid alternative to the existing SORS.

## Time-domain Diffuse Raman Spectroscopy (TD-DRS)

The aim of the work is to transfer the know-how developed in the last 20 years of Time-Domain Diffuse Optics (TD-DO) to the realm of Raman spectroscopy, to lay strong foundation by the theoretical and experimental realization of

TD-DRS. New analytical model in collaboration with the University of Florence was developed to answer the propagation of Raman photons in diffusive media. Unfortunately, the experimental realization of diffuse Raman is complex due to very low signal (factor of  $10^{-9}$  as compared to Tyndall scattering). However, a customized spectrometer and probe were built in our lab to enable the sequential detection of time resolved Raman photons, thereby opening to the horizons of TD-DRS. Furthermore, a new detector technology developed by PicoQuant was exploited to make parallel acquisition of TD-Raman curves. Preliminary results revealed feasibility of the TD-DRS measurement with single-photon counting and demonstrated depth sensitivity of the approach. This PhD dissertation was funded by OILTEBIA (Optical Imaging and Laser Techniques for Biomedical Applications). The author is a Marie Curie fellow funded by OILTEBIA project. The author takes opportunity to express his gratitude to his supervisor and tutor for their effective guidance, in general to the European Union for its role and support.



## SOLUTION PROCESSABLE CARBON NANOTUBES IN HYBRID ORGANIC SYSTEMS FOR ELECTRONIC APPLICATIONS

**Maqueira Albo Isis – Supervisor: Dr. Mario Caironi**

The recent years have been characterized by marvelous discoveries in new materials. After the silicon electronics revolution that jeopardized the scientific attention, the scientist's curiosity was directed onto the properties of unconventional materials, with their "smart" characteristics and deposition methods, and possible new application or unconventional uses for old-fashioned materials. From this, interesting materials and their properties have been discovered or reengineered: from the unpredicted performance of materials such as graphene to the realization of organic-based electronics, from raspberry juice, employed in DSSC solar cells, to the unexpected use of PET as substrate for electronics. One of this envisioning materials are carbon nanotubes, whose this thesis is about. Carbon nanotubes emerged during the 90s exhibiting outstanding electronic properties. Their tunable properties are very promising for high-performance carbon based electronics and will significantly contribute to brake the silicon hegemony.

This work, carried out at the Center for Nano Science and Technology of the Istituto Italiano di Tecnologia within the framework of the Marie Curie training actions, POCAONTAS1 project, proposes the use of solution processable nanotubes in hybrid organic electronics applications. We did study the role of cost-effective solution processed single-walled nanotubes as charge transport interlayers in solar cells, with an efficiency increase of 27% with respect to a reference bulk heterojunction solar cell without carbon nanotubes. Following, polymer/carbon nanotubes systems are studied in order to increase the thermoelectric properties of conjugated polymers: composites of PEDOT:PSS and multi-walled nanotubes showed an increment of the electrical conductivity, with respect to the starting material, in the presence of low loads of nanotubes. In this context, we proposed a novel approach and data modeling for the determination of the

thermal conductivity that opens the opportunity to fulfill the thermoelectric characterization of thin film materials, that still remains a challenge for the materials employed in the emerging field of organic electronics, using standard pump-probe setups. The last part of this work is related to the realization of fully-printed transistors comprising polymer-sorted CNTs. We bring a detailed study of the characteristics of the sorted materials by PFO-BPy polymer. The results obtained, with top FET mobility of the fully-printed devices approaching  $10 \text{ cm}^2/\text{V s}$ , places this work between the only few fully-printed devices based on carbon nanotubes networks. With these studies it is demonstrated the versatility of carbon nanotubes for electronic applications, going from the exploitation of their semiconducting character for OPV and FETs as well as their metallicity for organic thermoelectrics.

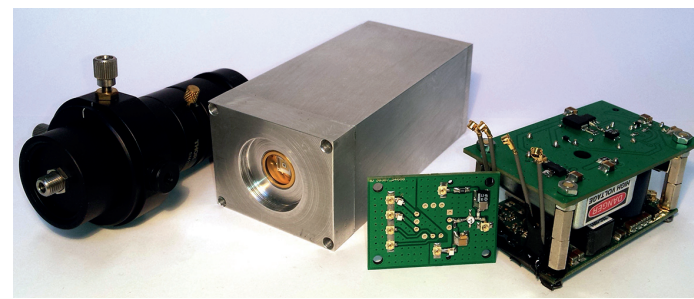
## DEVELOPMENT OF ACTUATED MORPHING STRUCTURES BASED ON COMPOSITE FLEXIBLE ELEMENTS.

**Martinenghi Edoardo – Supervisor: Prof. Alberto Dalla Mora**

What has always driven the evolution of mankind is the search for knowledge and, most of all, the attempt to understand Nature. Nature expresses itself as a multitude of complex mechanisms and processes that the human being had always tried to explain and interpret. What can be considered as more emblematic of Nature's complexity if not the human body itself? Hence, a growing number of methods were explored to study and decipher this complexity, leading in the last century to medical imaging, which is the seek to reveal internal structures keeping the subject alive and wealthy. The first experiments were performed by means of X-ray radiation; this solution had been widely developed thus leading to extremely precise and high resolution images. Different media or radiations are currently employed, therefore a wide scenario of alternative techniques had risen such as Ultrasounds Imaging, Magnetic Resonance Imaging (MRI) or Positron Emission Tomography (PET). However, all these techniques, either involve dangerous side effects, due to ionizing radiation, or require expensive and bulky instrumentation that hampers the use of these technique for

bedside monitoring or broad screening programs. Alternatively, light can be used as a radiation to explore the inside of the human body in a completely non-invasive way, for that reason optical imaging techniques were born in the last decades. Among them, there are either techniques based on fluorescence (such as Fluorescence Reflectance Imaging, FRI) or Diffuse Optics (DO). Traditionally DO makes use of a continuous laser source, which is injected into the sample, while the re-emitted light is re-collected at a certain distance  $r$ . Increasing that distance allows to probe deeper structures inside the sample. However, this approach is severely obstructed by the interaction between light absorption and scattering that leads to strong signal attenuation and poor spatial resolution. As an alternative, a Time Domain (TD) approach can be adopted, where one more dimension is introduced: the photon time-of-flight  $t$ . Hence, by means of a pulsed laser source in way of the CW one, absorption and scattering contribution can be uncoupled and the sample can be probed in depth by collecting long-lived, deep-travelling photons. Employing the TD approach can also lead to reduce  $r$  ideally down to zero, optimizing

light confinement into the sample and increasing both contrast and spatial resolution. To exploit this null source-detector distance approach an efficient gating mechanism is needed to extract the few number of "late photons", carrying the useful information about the sample deepest layers, out of the vast majority of "early photons" that can easily saturate the detector. The real limitations of TD as compared to CW systems are complexity and cost, which hamper the widespread diffusion of this technique in clinical environment and the design of wearable devices. Indeed, state-of-the-art TD-DO systems make use of expensive and bulky instrumentation such as PhotoMultiplier Tubes (PMTs), obsolete pulsed lasers and complex Time-Related Single-Photon Counting (TRSPC) electronics. With the exploration of novel photonics technologies and the design of new systems, this thesis work aims to set a considerable step in the evolution of TD-DO towards a future scenario where TD instrumentation can achieve the same technological level of the CW one, even though featuring impressively better performances both in terms of depth penetration and spatial resolution. In fact, state-of-the-art



**1. Picture of the SiPM module (center), with example of possible optics for fiber coupling (on the left) and the three electronic boards present in the instrument (on the right).**

CW-DO systems are nowadays extremely compact and cheap, employing well established technologies that easily allow the construction of multichannels and wearable devices, capable of extracting the best performances achievable with this technique. To achieve the performance breakthrough in TD-DO three key conditions need to be provided: (i) a dense distribution of compact sources allowing to increase the optical power injected into the sample; (ii) a dense distribution of detectors to increase the collection area, thus maximizing the photon harvesting; (iii) detectors need to be fast-gated to extract the "late Photons" contribution from the overwhelming number of "early" ones. During this thesis work the experimental activity was focused heading to this final targets.

In the first condition direction, we designed and validated, in collaboration with "Dipartimento di Elettronica, Informazione e Bioingegneria (DEIB) of Politecnico di Milano", a contact probe embedding a pulsed Vertical Cavity Surface Emitting Laser (VCSEL). The laser die dimensions are extremely small (less than 1 mm x 1 mm), therefore arrays embedding several tens of devices are already commercially available and can be employed to design compact and dense distributions of sources synchronously pulsed. To enable the second condition of dense detectors distribution, Silicon PhotoMultipliers (SiPMs) were introduced for the first time in TD-DO, obtaining impressive results thanks to an innovative design of the electronic systems needed to drive SiPMs. As an example, Figure 1 reports a

SiPM based instrument that we designed to be employed as fundamental module for the construction of TD-DO systems. Hence, embedding the SiPM module, multiple systems were designed and tested on field. The third condition presented was the availability of gateable detectors; to this purpose a proof of concept probe, embedding a fast-gated Single-Photon Avalanche Diode (SPAD) designed by DEIB, was developed and successfully validated together with the pulsed VCSEL both on phantoms and in-vivo. Considering that SiPMs are designed by parallelizing SPADs as elementary cells, this probe allows to foresee the advantage coming from the fast-gated operation of the whole SiPMs. In conclusion, by developing and testing new technologies in the field, this work has just opened the way towards a new class of devices with both performance and dimension breakthroughs, that will allow in the years to come the construction of wearable TD-DO systems for both clinical and consumer markets.

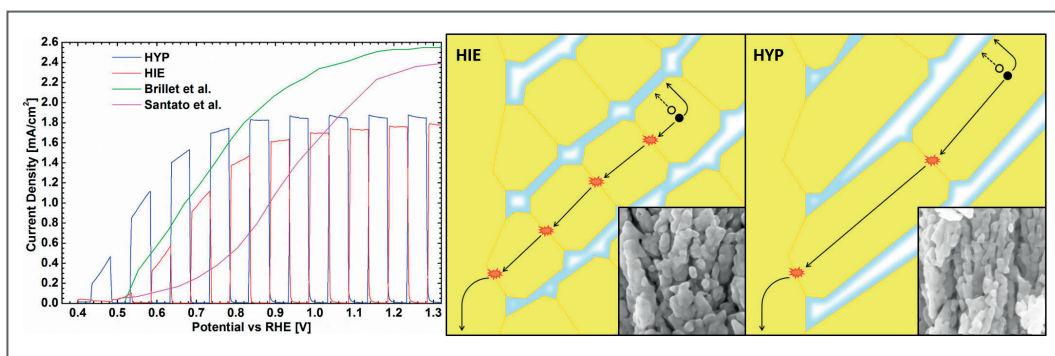
# NANOSTRUCTURED WO<sub>3</sub> FILMS FOR PHOTOELECTROCHEMICAL WATER-SPLITTING

Mezzetti Alessandro – Supervisor: Prof. Guglielmo Lanzani

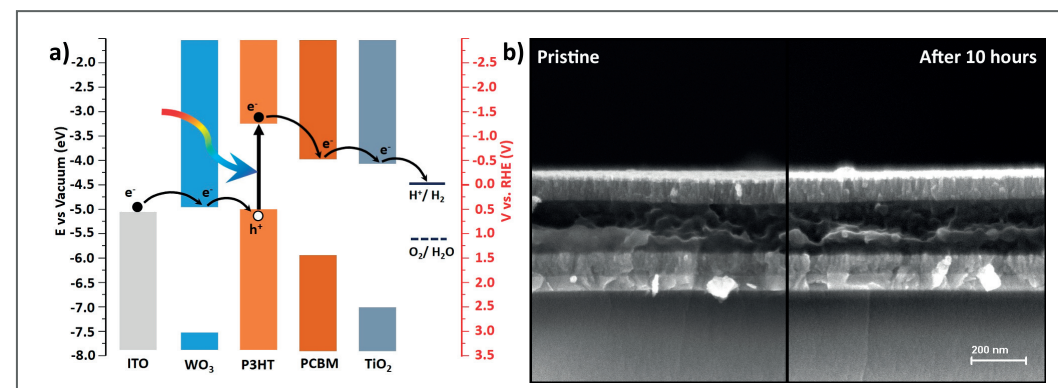
During the PhD program, I have focused my research on photoelectrochemical (PEC) water-splitting. The long-term vision behind this work is the production of hydrogen via solar energy to be used in the forthcoming hydrogen economy. In PEC water-splitting, the chemical energy required to cleave the water molecules is provided by solar photons, that are absorbed and converted by the photoelectrodes. Photoelectrodes are carefully designed semiconducting architectures that collect incoming photons and generate separated charges with the correct energy amount to drive the water oxidation and reduction reactions. Thermodynamic constraints impose an energy gap of at least 1.23 eV, but it experimentally increases due to overpotentials

and it must be properly aligned with respect of the reduction and oxidation potential of water. The process can be performed by a single photoelectrode, but in terms of optimization it is more reasonable to separate the two half-reactions and ascribe them to their specific device, photoanode for the oxygen evolution and photocathode for the hydrogen evolution. In these three years, I have contributed in the fabrication, characterization and optimization of photoelectrodes made with WO<sub>3</sub> films: quasi-1D hyperbranched WO<sub>3</sub> photoanodes and amorphous WO<sub>3</sub> hole selective layer for hybrid organic photocathodes. Quasi-1D hyperbranched WO<sub>3</sub> photoanodes are fabricated via pulsed laser deposition through a self-assembly process from

the gas phase, obtaining arrays of tree-like nanostructures with strong directional growth, high crystallinity and improved long-range order. The PEC characterization of these photoanodes exhibits an onset potential as low as 0.4 V<sub>VRHE</sub> and saturation current densities up to 1.85 mA·cm<sup>-2</sup> at 0.8 V<sub>VRHE</sub>. While the saturation photocurrent values are similar to the state-of-the-art values for WO<sub>3</sub> photoanodes, both the onset and saturation voltages are significantly lower than any other reported values. Further investigation attributes these low voltage values to the efficient charge generation, charge injection and charge transport. The hyperbranched morphology absorbs and converts incoming photons, up to wavelengths close to the WO<sub>3</sub> band-edge cutoff.



1. LSV curves (right) of the HIE and HYP best-performing samples, against state-of-the-art WO<sub>3</sub> photoanodes. Schematic (left) of the electron and hole extraction process within the HIE and HYP crystalline morphology.



2. Energy level diagram (a) of the hybrid organic photocathode, showing the steps of electron injection process. SEM cross-sectional images (b) of the hybrid organic photocathode, pristine and after 10 hours of uninterrupted operation, showing no signs of film degradation for any composing layer.

Thanks to the nano-tree structure, holes have to travel only through the width of the crystallites to reach the electrolyte, a distance significantly lower than the hole recombination length in WO<sub>3</sub>. At the same time, electrons have to travel along the whole nano-tree structure, but are facilitated in the process by the strong directional growth and high crystallinity, that provide few interfacial boundaries and lattice defects where the electrons might undergo trapping or recombination events. These effects are confirmed by comparing the characterization of the optimized hyperbranched morphology – labelled as HYP – with a similar hierarchical nano-tree structure – labelled as HIE – that lacks the improved long-range order and strong crystalline directional growth. Hybrid organic photoelectrochemical (HOPEC) devices exploit the use of organic semiconductors as photoactive materials, as already demonstrated by organic photovoltaics (OPV). To

achieve high performances, the organic semiconductor needs to be coupled with selective contacts that efficiently extract the charges. Finding the correct material for the selective contacts is currently one of the main research topic in the field, since both the optoelectronic requirements of OPV as well as the electrochemical constraints of standard PEC need to be satisfied. Correct energetic alignment is fundamental to separate the photogenerated charges, as well as the capability to selectively inject only the correct type of charge to reduce recombination and parasitic currents. Furthermore, selective contacts need to be transparent to avoid shadowing the absorption of the organic photoactive material and must display strong electrochemical stability in order to perform durably in the electrolytic environment. TiO<sub>2</sub> satisfies these requirements and is the materials of choice to cover the role of the electron selective layer (ESL). Conversely,

finding the appropriate material for the hole selective layer (HSL) have been proven to be much less straightforward. Based on previous HOPEC architectures that use P3HT:PCBM blend as the photoactive material and an amorphous TiO<sub>2</sub> film as the ESL, an amorphous WO<sub>3</sub> film deposited via reactive magnetron sputtering is employed as the HSL in order to exploit of the strong chemical stability of WO<sub>3</sub> and thus obtain longer lifetimes while retaining adequate operational performances. The resulting photocathode achieves a photocurrent of 2.48 mA·cm<sup>-2</sup> at 0 V<sub>VRHE</sub>, an onset potential of +0.56 V<sub>VRHE</sub> and a state-of-the-art operational activity of more than 10 hours.

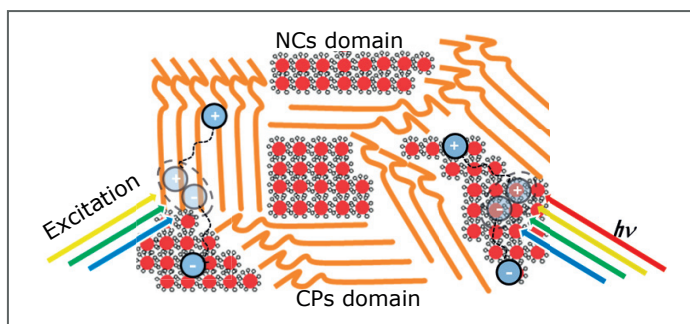
# ULTRAFAST CHARACTERIZATION OF HYBRID NANOCOMPOSITES FOR ENERGY PRODUCTION AND OPTICAL SWITCHING

**Moretti Luca** – Supervisor: Prof. Francesco Scotognella

Conjugated Polymers (CPs) and Semiconductor Nanocrystals (NCs) are two classes of materials well studied in literature nowadays. They have been used for different types of application. Although the implications of mixing them with other organic or inorganic materials have not been unravelled yet. The possibility to combine different properties brings to the achievement of various possible tasks for technological applications. By using materials activated by external stimuli it is possible to tune the visible absorption of CPs and therefore exploit them in solutions for light manipulation, such as in telecommunication systems or smart windows. CPs are also well known for their use in photovoltaic devices, in all organic bulk heterojunctions for example. An interesting perspective is to blend CPs and NCs in order to take advantage of optical and electronic properties of both of them. NCs show also plasmonic behaviour depending on their shapes and environmental conditions. They are therefore used in sensing applications and in close vicinity with other types of compound. An emerging field of study is to exploit the plasmonic resonance for enhancing the photo-catalytic effect of metal materials.

This thesis is dedicated to the study of hybrid compounds of CP and NC by means of ultrafast transient absorption spectroscopy. The main aim is to understand the implication of the micro- and nano-scale interaction between the materials regarding the resulting effect on the de-excitation path of the optically excited species, excitons or charges generated by means of absorption of light radiation. The more important nanocomposites that have been studied are the following. A mixture of F8BT and 5CB has been studied in order to achieve a novel electro-optic effect of the compound. The emission of this light-emitting polymer (F8BT) is usually hidden by the formation of charge transfer states. This has always been

an issue and different types of solution have been proposed. By exploiting the possibility to control the alignment of the nematic liquid crystal (5CB) we wanted to be able to control the emission of the polymer itself. By means of ultrafast pump-probe spectroscopy we thus observed a modulation of the stimulated emission (SE) of the F8BT, driven by the external applied voltage. We attribute the rise of the SE to a rearrangement of the polymer that modifies its packing. The alignment of the LCs under the external bias changes the inter-chain interactions in the F8BT, in turn effecting the deactivation pathways of the photoexcited state. In particular the quenching of charge generation leads also to a longer lived SE. This effect occurs above a threshold of the



**1. Schematization of the hybrid CP/NC nanocomposite with excitons formation and consequent dissociation: transfer of electron from CP to NC domain and charge generation in the NC domain**

electric field amplitude related to the LC orientation dynamics, the so called Fréedericksz transition. In the end we basically demonstrated a new electro-optical effect: the electric field induced switching of SE in a blend of F8BT/5CB. This field induced stimulated emission modulation can find application in information and communication technology, lasing and optical sensing. The idea around the second category of nanocomposite studied is to exploit both the large visible absorption and mechanical flexibility of CP and the high transport properties, stability and IR absorption of NC in photovoltaic applications. The first blend studied is based on P3HT polymers and lead sulphide (PbS) nanocrystals. This sample was treated by tailoring nanocrystal surface chemistry, allowing to control noncovalent and electronic interactions between organic and inorganic components. The pending moieties of organic ligands at the semiconductor NC surface were shown to hinder charge separation and transport, drastically impacting on morphology of hybrid nanocomposites during formation from blend solutions. The importance of this approach was demonstrated by the fabrication of hybrid solar cells displaying a power conversion efficiency that reaches 3%. Arenethiolate ligands promote phase segregation at the nanometer size scale between the two components, yielding a hybrid nanocomposite that displays distinct domains, with dimensions comparable to the charge carrier

and exciton diffusion lengths in solids of the pure separated materials. This nanoscale arrangement allows electron-hole pairs photo-generated in the P3HT domain to reach the extended hybrid interfacial area where they could separate in long-lived charge carriers which are expected to get to the electrodes via eventual percolating paths, although partial recombination occurs. By investigating time-resolved photo-induced processes in the nanocomposites and their single constituents, we determined that electron transfer occurs at the hybrid interface, while hole transfer appears to be prohibited. Stated this behaviour we carried on further studies by mean of changing the polymer blended in the nanocomposite: MEH-PPV and PTB7 were compared to P3HT. Comparisons between resonant and non-resonant pumping with both the materials reveal a trend in the efficiency of electron transfer from the CP domain to the NC one. Higher band gap polymers show a more efficient hot transfer towards the nanocrystals energy levels. To sum up, a reliable path aiming to gain control over macroscopic optoelectronic properties of polymer/nanocrystal composites is offered along with a study of the most efficient electronic band coupling between the two material, thus contributing to suggest novel pathways towards efficient CP/NC solution-processed hybrid solar cells, which still stays behind the efficiencies obtained for devices based on pure polymer and nanocrystal active layers.

The exploitation of the plasmonic behaviour of NC was studied here for photocatalysis application in semiconductor-metal hybrid nanostructures that offer a highly controllable platform for light-induced charge separation, with direct relevance for their implementation. Control in the synthesis over the size, shape and morphology of the nanocomposites provide tunability of the optical and electronic properties. We studied a well-defined model system of cadmium sulphide-gold nanorods (NRs), by focusing on the effect of the gold tip size on the photocatalytic function due to the fact that the metal domain characteristics are a critical determining factor of the photocatalytic cycle. By means of transient absorption measurements we studied the charge transfer dynamics from the NRs to the metal, providing an additional information that, along with hydrogen evolution kinetics and theoretical modelling, revealed a non-monotonic behaviour with size of the gold tip. The optimal metal-domain size value is explained in terms of competing processes of electron injection to the metal tip and water reduction on the metal surface. This behaviour is furthermore general and not limited to the metal type or the reduction reaction, and can be used for rational design of photocatalysts based on hybrid semiconductor-metal nanostructures.



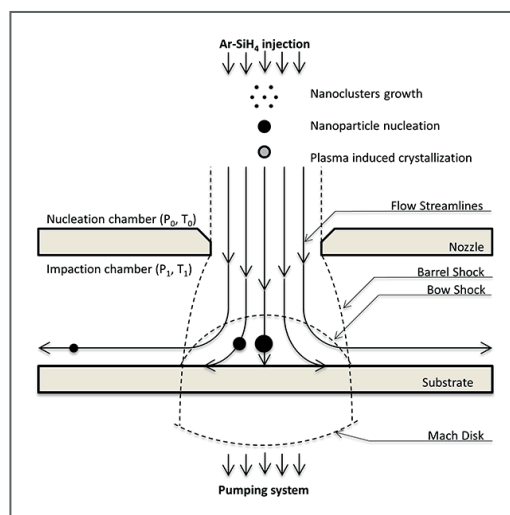
# NANOPARTICLE JET DEPOSITION. A NOVEL PLASMA-BASED APPROACH FOR ROOM-TEMPERATURE, HIGH-THROUGHPUT AND LARGE AREA SYNTHESIS OF NANOSTRUCTURED MATERIALS

Nava Giorgio – Supervisor: Dr. Fabio Di Fonzo

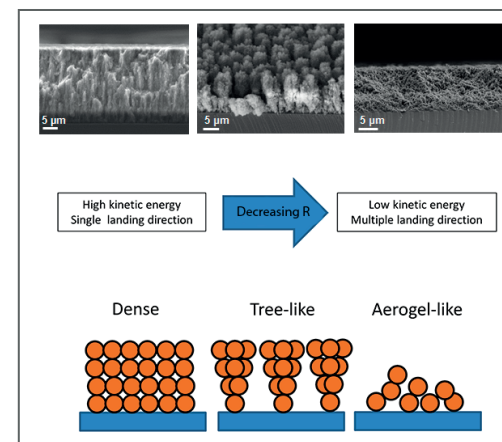
In the last decades silicon-based nano-materials attracted great interest mainly due to their intriguing and size tunable properties, markedly enlarging their areas of application with respect to their bulk counterpart. Depending on the number of dimensions confined at the nanoscale size, silicon nanostructures can be roughly classified in three categories: 0-dimensional (0-D), 1-dimensional (1-D) and 2-dimensional (2-D) systems. Among the 0-D silicon nano-materials, silicon quantum dots arguably represent the most investigated structures. When silicon crystallites size is reduced below the Bohr exciton radius (around 5 nm), an intense light emission with size-tunable

wavelength is induced in the material, phenomenon exploited for the fabrication of silicon LED (SiLED). 1-D and quasi 1-D silicon structures, such as nanowires, nanotubes and nanotrees, exhibit facile charge carriers transport and tunable porosity, thus making them an appealing candidate as active layers in high capacity lithium ion battery anodes. Among 2-D nanostructures, hydrogenated nanocrystalline silicon thin films, with enhanced charge carriers mobility and light stability upon light exposure, are considered a promising alternative with respect to the widely employed hydrogenated amorphous silicon, currently material of choice for several large area microelectronics applications (e.g. LCD screens).

Despite a high number of fundamental investigations on silicon nanostructured materials properties and their successful integration in high-performance devices, a comparatively smaller attention was dedicated to the means of their synthesis, with current lab-scale methods either not compliant to industrial requirements or characterized by high processing temperatures, not compatible with the use of cheap flexible polymeric substrates. The Ph.D. work of the author was focused on the development of a novel large area (100 cm<sup>2</sup>), high-throughput (up to 20 nm s<sup>-1</sup> or 300 mg h<sup>-1</sup>), room-temperature, plasma-based synthesis technique for nanoparticle-assembled silicon films production with controlled crystalline volume fraction, particle size and morphology/porosity. The process is based on the segmentation of the gas phase material synthesis in two steps (see Figure 1): (i) nanoparticles in-flight synthesis, growth and low-temperature crystallization control in a non-thermal dusty plasma environment (nucleation chamber, at a pressure  $P_0$  and temperature  $T_0$ ); (ii) nanoparticle-assembled films ballistic growth via supersonic jet acceleration (impaction chamber, at a pressure  $P_1$  and temperature  $T_1$ ). A high aspect ratio rectangular nozzle divides



1. Schematics of the NanoJeD synthesis apparatus.



2. Morphologies fabricated for decreasing R values with NanoJeD technique. At high R values mono-directional high kinetic energy impaction of nanoparticles takes place, while for decreasing R, particle velocity is reduced and landing direction randomized.

the nucleation chamber from the impaction chamber (connected to a turbo pump) maintaining a pressure ratio  $R = P_0/P_1$  between the two stages and allowing, for  $R > 5$ , the formation of a highly under expanded supersonic jet in the impaction chamber. A low pressure non-thermal RF plasma discharge is ignited in the nucleation chamber in an Ar-SiH<sub>4</sub> gas mixture. The plasma environment efficiently dissociates the silicon precursor (SiH<sub>4</sub>) promoting in flight nucleation and plasma-induced crystallization of silicon nanoparticles. Silicon nano-materials with crystalline volume fractions ranging from 0% to 72%, controlled by tuning the value of the RF power coupled in the plasma discharge, and nanoparticle sizes in the range from 2 nm to 5.5 nm, controlled by varying the total gas flow rate, can be synthesized in the nucleation stage. Given the continuous flow structure of the described system, the nucleated nanoparticles are dragged and accelerated by the supersonic jet, finally landing on a substrate placed in the impaction chamber. Control over synthesized

material morphology is achieved by tuning the flow field of the supersonic jet, controlled by the R value (see Figure 2). By reducing R, morphology can be varied from dense, to nanostructured tree-like down to aerogel-like and correspondingly density is reduced from 50% (maximum theoretical density for a closely packed aggregate of mono-disperse spheres) down to 5%, without affecting the nucleation chamber conditions (the nozzle, in choked flow condition, decouples the nucleation stage from the impaction stage). The NanoJeD synthesized silicon nanostructured materials were investigated during the Ph.D. activity of the author for applications in the fields of flexible electronics and lithium ion battery anodes. Dense highly crystalline nanoparticles-assembled films were studied for their charge carrier transport properties via transient photocurrent time of flight spectroscopy (TOF). The measured photocurrents highlighted an anomalous and dispersive charge carrier transport with balanced mobility values up

to  $1.2 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , highest value reported in literature for a silicon nanoparticles-assembled film deposited at room-temperature. The material was further tested for the fabrication of proof-of-concept field effect transistors, demonstrating the presence of a genuine field effect current modulation and the possible application of NanoJeD technique in the emerging field of flexible electronics. Freestanding amorphous silicon nano-powders (7 nm average particle size) were synthesized by NanoJeD method and tested for the slurry fabrication of lithium ion battery anodes. A mixture of silicon nanoparticle, poly acrylic acid and carbon black, was drop casted on a copper collector and annealed at 750° in a nitrogen atmosphere (the pyrolysis of the polymer thus resulted in the formation of conductive porous carbon matrix). The small dimensions of the NanoJeD synthesized particles, not within the reach of state-of-the-art powder production systems, ensured a stable lithiation-delithiation process of the silicon material with no cracking, resulting in high and reversible charge storage capacity (1000 mA h g<sup>-1</sup> and up to 300 cycles). Finally, light management properties of nanostructured silicon thin films and silicon multilayers with periodic variation of porosity were investigated.

## DEVICE OPTIMIZATION FOR GRAPHENE HIGH FREQUENCY TRANSISTORS: FROM CVD GRAPHENE TO HBN/G/HBN HETEROSTRUCTURES

**Pedrinazzi Paolo** – Supervisor: Prof. Roman Sordan

Two-dimensional materials, such as graphene,  $\text{MoS}_2$  or  $\text{WSe}_2$ , represent a new paradigm in thin-film transistor technology, providing also the opportunity for new device concepts. Graphene is one of the possible contenders in high-frequency electronics, mainly due to its high charge carrier mobility and velocity saturation, which exceed that of conventional high-mobility semiconductors (III-V or SiGe). Scalable production techniques, such as chemical vapour deposition (CVD), can now deliver graphene on a large scale which is interesting from the industrial point of view. However, fabrication of graphene field-effect transistors (GFETs) needs further development if graphene is to compete with established semiconductor technologies. One of the main parameters degrading high-frequency response of GFETs is contact resistance, which should be reduced below 100  $\text{W}\mu\text{m}$  to reach that of conventional high-frequency transistors. During my PhD studies I successfully demonstrated graphene/metal contacts with a typical contact resistance below 80  $\text{W}\mu\text{m}$  at the Dirac point. The contact resistance was determined by transmission line measurements (TLMs) at room temperature. The low contact resistance was

obtained by etching holes in CVD-grown graphene channel before the deposition of contacts. This increases the contact edge with metal contacts deposited on top and therefore the injection of carriers through the graphene edge. Such ultra-low contact resistance is comparable to that of InP THz transistors and provides a viable route to high-frequency GFETs. The benefits and improvements in graphene technology were tested through the fabrication and characterization of high frequency GFETs: I designed and fabricated these devices using CVD grown graphene as a channel material transferred on a 1  $\mu\text{m}$  thick  $\text{SiO}_2$  substrate. Different materials and designs were electrically tested: we used  $\text{AlO}_x$  as a top gate dielectric in all transistors while changing the metal contacts and layouts. We obtained the record high  $f_{\text{max}}/f_t$  in GFETs, demonstrating that graphene transistor technology can compete with well-established technologies. Here,  $f_{\text{max}}$  is the maximum frequency of oscillation and  $f_t$  is the cutoff frequency. In order to further improve the frequency response of the GFETs I investigated alternative thin gate oxides, such as  $\text{TiO}_x$  and  $\text{HfO}_x$ , because they have very large dielectric constants. To this end,

graphene inverters were realized in which the lowest contact resistance obtained previously was implemented. Due to a lack of a proper growing method,  $\text{HfO}_x$  did not provide any benefits while  $\text{TiO}_x$  provided interesting and promising results. However, high leakage currents in GFETs with  $\text{TiO}_x$  gate oxide requires further investigations which should open a path to further improvements. One of the main limitations of graphene in technological applications is the reduction of its mobility exhibited in realistic devices. As exfoliated, graphene does not have the high mobility which is theoretically predicted. For this reason, I then studied alternative substrates for GFETs which should increase mobility by suppressing the substrate induced scattering. First, I focused on STO (strontium titanate) as a high-k substrate/gate oxide for graphene (140 nm crystalline STO layer was grown on top of a conductive LSMO layer). I fabricated and characterized GFETs and graphene inverters on such substrates. Maximum transconductance around 600  $\mu\text{S}/\mu\text{m}$  and DC voltage gain around 5 at a gate length of 2  $\mu\text{m}$  were obtained, showing good electronic properties of GFETs fabricated on STO substrates. However, since mobility in these

GFETs was still very low and gate leakage currents high, research on another type of substrate, namely hBN (hexagonal boron nitride) was initiated. Research on hBN substrates led to very preliminary but interesting results which need further investigations. The benefits of this material as a substrate for graphene have been widely demonstrated in literature, but not in more complex graphene devices and circuits. Further improvements in this research field were attained during the period I spent in the Nanocarbon Group of the Denmark Technical University, Copenhagen, where my research was focused on the fabrication and characterization of Van der Waals heterostructures of graphene and hBN. Thanks to the stacking technique developed in this group, I developed my own procedure capable of realizing hBN/graphene/hBN heterostructures in which the thickness of the top hBN layer was below 8nm, preserving at the same time the improvement of the electrical properties provided by such encapsulation. Both Raman and electrical characterizations were performed on these devices, first for a pre-selection of the high-quality areas for the fabrication of final devices and second to link the optical and electronic

properties as a test of the technological improvements. The heterostructures were electrically characterized, from room to cryogenic temperatures (4 K). Another achieved objective was the large obtained quantity (and quality) of doping-homogeneous stacks (doping concentration  $< 10^{12} \text{ cm}^{-2}$ ) with large mobility of graphene ( $\sim 25000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  at room temperature) and with a very thin top hBN. With thicker top hBN, I consistently obtained graphene mobilities between 30000 and 50000  $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$  (at room temperature), which were measured by the Van der Pauw method. This reflects the method optimizations I performed, leading to a more stable technology (for the graphene encapsulation) and to more scalable fabrication. From a technological point of view, these first studies on thin hBN are quite interesting and important because the implementation of thin hBN as a top gate insulator is one of the main goals of the state-of-the-art graphene electronics. We also observed high leakage currents through thin top hBN gates at room temperature. Comparing to other studies, we discovered that it is possible to have defect mediated temperature-dependent leakage currents through a low number of hBN layers. We

therefore demonstrated that it is not possible to use hBN thinner than 10 nm as a thin top gate insulator at room temperature, because such layers have leakage resistance around 80-100 M $\Omega$ . We also found that leakage currents decrease when temperature decreases, resulting in good gate insulation only at cryogenic temperatures. The presented studies open path to new research projects. From a “graphene electronics” point of view, the future ideas are to implement these developments in the realization of more complex electronic devices and circuits, such as graphene inverters and ring oscillators. The purpose is to increase performances of already demonstrated devices by replacing CVD graphene (channel material) with high-mobility encapsulated graphene and using hBN as a top gate insulator (with some additions of  $\text{AlO}_x$  on top of hBN to prevent leakage currents). This also implies other studies, for example of contact resistance, which is now incompatible with the requirements for high frequency transistor operation. Finally, these studies should allow better understanding of required improvements of graphene high-frequency devices, both from a technological and fundamental point of view.

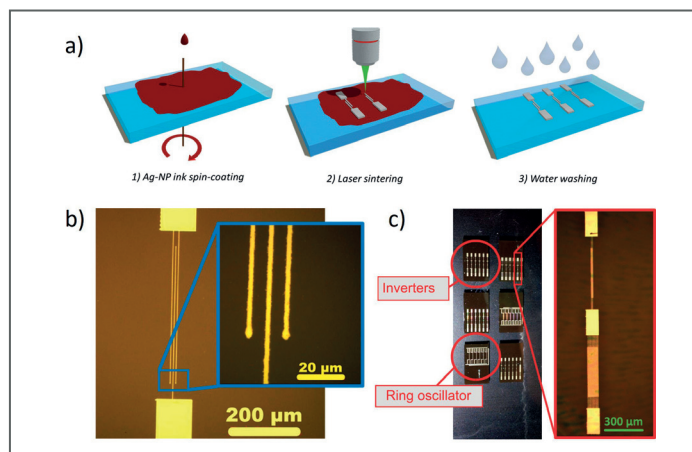
# HIGH-FREQUENCY ORGANIC FIELD-EFFECT TRANSISTORS BY LOW-COST DIRECT-WRITING AND PRINTING TECHNIQUES

Perinot Andrea – Supervisor: Prof. Mario Caironi

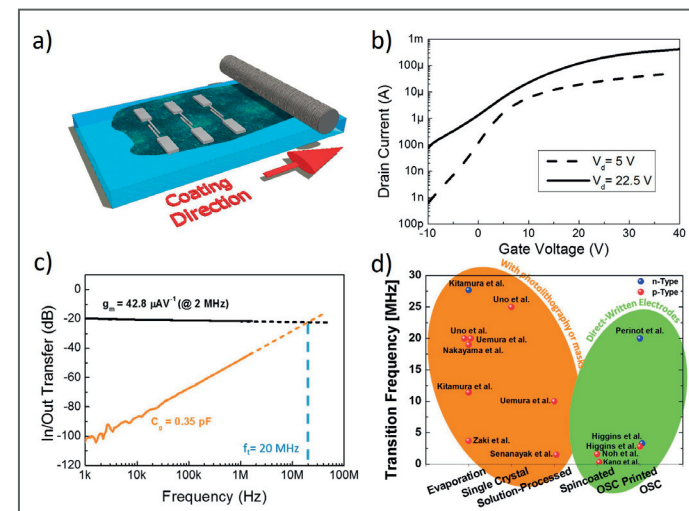
The evolution of the electronic technologies has always been driven by the constant emergence of new applicative fields, leading to an ever-increasing number of commodities integrating an electronic functionality. Nowadays, a powerful request is evolving for cost-effective, lightweight, portable and distributed electronic devices. The development of a suitable technology capable of delivering such features would open the way to the implementation of a myriad of applications in the fields of wearables, healthcare, goods monitoring, logistics and sensors. Printed organic electronics is a powerful candidate to comply with the needed requirements of reduced cost and compatibility with flexible and conformable substrates. The possibility of depositing functional materials from solution enables the use of printing techniques, which belong to a widespread and mature technology perfected along many centuries. This approach potentially offers a low-cost, high-throughput production process, compatible with a wide range of conformable substrates. Additionally, direct-writing techniques, allowing for the deposition of functional materials following a digital layout, combine the phases of material transfer and patterning in one

single process step, guaranteeing fast processing with reduced waste: laser processing and inkjet printing are well-known and widely adopted, not only by the specialized industry. The vast flexibility in the synthesis and in the tuning of solutions rheology properties offered by polymers makes the adoption of these semiconductors an excellent choice for the realization of devices using materials with optimal processability and ever-increasing performance. The combination of these techniques and materials for the fabrication of OFETs, the basic building block of complex circuits, has already been widely demonstrated in

the literature with increasingly improving figures of merit. Nonetheless, it is a generally acknowledged that, to enable additional desirable features for a wide range of applications (e.g. RFID communication) and to facilitate the integration of multiple functionalities (e.g. integrated driving circuitry for high-resolution displays) with a fully-printed approach, the operational frequency of the OFETs must overcome a threshold conventionally set to 10 MHz. However, the maximum operational frequency of OFET devices is still generally limited: to date, the achievement of operational frequencies in excess



1. a) Schematic of the laser sintering process steps.  
b) Laser-sintered, high-resolution conductive electrodes for OFETs.  
c) Laser sintered patterns for organic circuits.



2. a) Schematic of the bar-coating printing technique adopted for the deposition of a high-effective mobility semiconductor layer over a wide area. b) Static transfer curves for an OFET with a highly scaled channel length ( $L = 1.75 \mu\text{m}$ ) realized on laser-sintered, high-resolution electrodes. c) Measurement of the transition frequency of direct-written and printed high-frequency OFETs integrating laser sintered electrodes and bar-coated semiconductors. d) Comparison of selected works in which the transition frequency was measured directly, classified with respect to the adopted fabrication methods.

of 10 MHz has mainly relied on the use of complex photolithographic and/or evaporation techniques, undermining the whole concept. Therefore, a huge interest in the development of new techniques is driving the research for new cost-effective processes for the achievement of high-frequency OFETs. The combination of direct-writing and printing techniques constitutes a powerful candidate, combining the corresponding advantages of each method and offering a fully solution-based and mask-less approach. The motivation of this work is the realization of high-frequency OFETs solely adopting such combination, demonstrating the applicability of a fully mask-less

and solution based process as an upscalable candidate for mass production of these devices. Initially, we characterized fs-laser sintering, a direct-writing technique for the definition of high-resolution features (in the range 1-2 μm) on glass and on flexible PEN substrate. The realized Ag features exhibited conductivity not far from the one generally obtained with conventional printing and sintering techniques, and well suitable for the use into OFETs. We integrated this process with the capability of multilayer processing (i.e. the vertical stacking of independent layers). We then demonstrated high-frequency operation of direct-

written and printed n-type OFETs. We optimized the injection properties for the OFETs and obtained an effective charge mobility in excess of  $0.8 \text{ cm}^2/\text{Vs}$  for a channel length  $L = 1.75 \mu\text{m}$ . Overall, these aspects led to a transition frequency  $f_t = 20 \text{ MHz}$ , the highest to date for printed polymers and direct-written electrodes. We then tested the applicability of the same process in the case of p-type devices, which need a contact treatment (a PFDT-based SAM) to enhance the scarce hole injection properties from Ag metal into the semiconductor. We tested different semiconducting materials and finally determined the frequency performance of devices featuring  $L = 1 \mu\text{m}$ , yielding a maximum  $f_t = 3.7 \text{ MHz}$ . Furthermore, we demonstrated that this technique can be also applied to a flexible substrate, and we realized OFETs with the same direct-writing and printing approach to yield n-type and p-type devices featuring  $f_t = 0.96 \text{ MHz}$  and  $f_t = 3.4 \text{ MHz}$  respectively. Finally, we addressed peculiar non-idealities in the frequency behavior of OFETs of this kind. We highlighted how additional accumulated charge in regions outside the nominal channel area adds a parasitic capacitive component degrading the frequency performance of the devices, and used a distributed-RC model to explain the features observed in the measurements. We proposed a simple double-drain approach to solve this problem, and tested the validity of our method in devices integrating high-resolution laser-sintered electrodes.



# ULTRAFAST SPECTROSCOPY OF LOW-DIMENSIONAL MATERIALS

Pogna Eva Arianna Aurelia – Supervisor: Prof. Giulio Cerullo

This thesis explores the optical properties of two-dimensional crystals by means of time-resolved spectroscopic techniques.

Two-dimensional (2D) crystals are atomically thin materials consisting of planes of atoms held together by strong covalent bonding to form layers, which, conversely, are stacked by much weaker van-der-Waals forces. The strong quantum confinement induces changes of the electronic band structure and optical behavior of isolated single layers (1L), giving rise to exciting and yet unexplored physical effects.

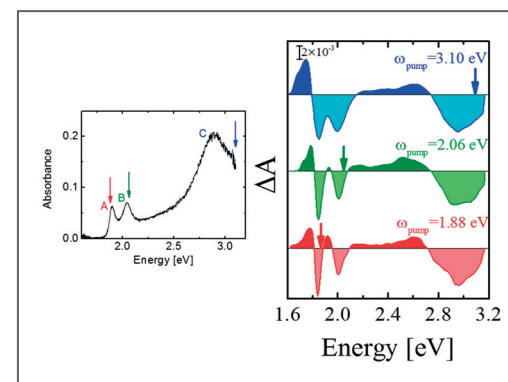
By far the most studied 2D crystal is graphene: 1L of carbon atoms arranged into a honeycomb structure. It is a semimetal, endowed with extraordinary sheet resistance, carrier mobility and conductivity. However, the absence of an electronic band gap has hindered its application in optoelectronics, motivating the search for alternative semiconducting 2D crystals. Among the layered materials, transition metal dichalcogenides (TMDs) are the most promising candidates to substitute graphene, in particular, compounds of molybdenum and tungsten. These latter are indirect-gap semiconductors which become direct gap in the

1L limit.

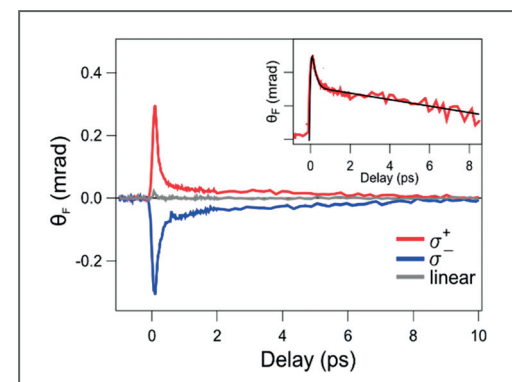
We have performed a study of the non-equilibrium optical properties of 1L-MoS<sub>2</sub> whose response is shared by the other semiconducting TMDs. We measured the transient absorption (DA) over a broad spectral range in order to monitor simultaneously three excitonic resonances in the visible range, labeled as A, B and C in Figure 1. To this aim, the standard transient absorption setup has been coupled with a confocal microscope, which enables to identify micrometer-size samples. Transient absorption spectra, at 100-fs time delay after excitation, are reported in **Figure 1**. After the photo-excitation, the excitonic resonances are bleached (DA<0) and red-shifted absorptions (DA>0) appear, independent of the pump energy. The comparison with ab-initio simulations enables to explain the experimental response in terms of energy renormalization of both the electronic band gap ( $E_g$ ) and the exciton binding energies ( $E_{b,\lambda}$ ). The combination of these two results in a few meV red-shift of the absorption, referred to as bandgap renormalization (BGR). This phenomenon has been observed in bulk systems but at much higher photo-excited carrier densities and it is enhanced in

2D crystals because of both the reduced dielectric screening and the quantum confinement.

A further evidence of the impact of dimensionality on 1L-MoS<sub>2</sub> optical response, is the relaxation dynamics of valley polarization. The electronic gap in 1L-TMDs appears at two different valleys, at K and K' points of the Brillouin zone. Because of the breaking of spatial inversion symmetry, valley and spin degrees of freedom are strongly coupled and, by means of circular polarized light, the two different valleys can be selectively populated, inducing valley polarization. We investigate the relaxation dynamics of the valley polarization by a combination of two non-equilibrium optical techniques: time-resolved Faraday rotation (TRFR) and time-resolved circular dichroism (TRCD). In the TRCD, the sample is excited with a circularly polarized pulse, resonant with the optical gap to induce the valley polarization, and we measure the transient transmittivity ( $\Delta T/T$ ) of co- and counter- circularly polarized pulses, probing the same and opposite valley. In TRFR experiments, instead, the relaxation is monitored measuring the rotation of the linear polarization of a probe pulse whose energy is tuned well below the absorption gap.



1. (on the left) Static absorbance of MoS<sub>2</sub>-1L and schematic of the BGR; (on the right) Transient absorption spectra at 100 fs after excitation with pump energy  $\omega_{\text{pump}}$  (see the arrows)



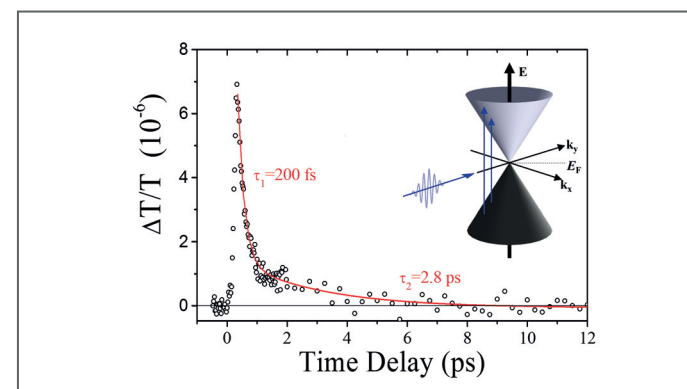
2. (left) TRFR traces with different pump polarization: -left and right circular (red and blue curves) and linear (grey curve), which allows to populate the K and K' valley and both of them respectively

In these conditions, the signals are only sensitive to intervalley scattering. Both techniques report similar relaxation dynamics (see the TRFR traces in **Figure 2**). The fast depolarization is attributed to efficient electron-hole Coulomb exchange interaction, a further proof of the enhancement of many body interactions in low dimensional materials. Beyond the field of 2D crystals, isolated layers can also be

reassembled into van der Waals heterostructures, made by stacking atomic planes in a chosen sequence. Among them, graphene encapsulation by hexagonal boron nitride (hBN) has demonstrated successful in decreasing the defects density and doping of graphene, improving its electrical properties. We have studied the optical properties of this heterostructure using high sensitivity transient

absorption. When graphene absorbs light, a distribution of hot electrons is created, whose cooling dynamics is strongly influenced by the phononic properties of the encapsulant material. Specifically, high-momentum hyperbolic phonons in hBN facilitate efficient near-field energy transfer from graphene, boosting the electron cooling, which is completed within few ps (see **Figure 3**).

An introductory chapter presents the fundamental physical properties of graphene and 2D transition metal dichalcogenides according to the state of the art. Methods and experimental setups developed during the thesis are also discussed. The body of the text concentrates on the published results on charge and spin carriers dynamics in MoS<sub>2</sub> and on the hot electrons relaxation in encapsulated graphene.



3. (down) Transient transmittivity of 0.95 eV probe after excitation with 1.55eV pump. (inset) Schematics of the excitation of electrons at graphene Dirac cone



# ULTRAFAST EXCITON DYNAMICS AND DUAL EMISSION IN SEMICONDUCTOR NANOCRYSTALS

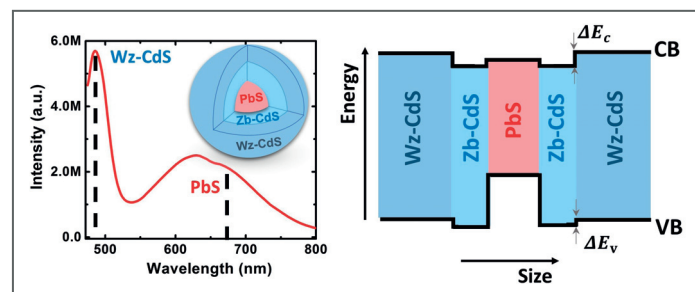
Sirigu Gianluca – Supervisor: Prof. Margherita Zavelani-Rossi

Colloidal semiconductor nanocrystals (NC) are nanometer sized materials composed by several hundreds of atoms. Their increasing attention in photonics is related to the possibility to synthesize them by low-cost techniques and to their interesting optical and electrical properties, like high photoluminescence quantum yield, high photo-thermal stability, low thermal conductivity and tunable energy bandgap controlled by nanoparticle size (quantum confinement effect). Specific interest is devoted to two-color emitting NCs for applications spreading from white LED to sensors based on ratiometric fluorescence for the ultrasensitive self-calibrating detection of local temperature, ionic species and pH. Dual emission arising from a single nanoparticle is particularly advantageous because it includes an internal reference which allows the reduction of the influence of external environment. Two different strategies can be exploited to obtain dual photoluminescence (PL) from a single NCs: by the employ of engineered heterostructures like core/shell NCs or by the NC doping with Mn or Cu.

A core/shell heterostructure can be engineered changing the

core and the shell dimensions, the material, the shape and the interface between core and shell and making multiple shells. While the process that leads to dual emission from a core/multiple shell structure is well known, this mechanism is still debated for a core/single shell structure. We have analysed the case of core/shell NCs with thin or giant shell. In this latter case we can distinguish heterostructures with graded or sharp interface. Generally core/shell structures with thin shell or graded interface show a single emission, while NCs with giant shell but sharp interface can emit double PL. These heterostructures have been optically characterized by ultrafast differential transmission (DT) and PL measurements changing the pumping conditions. PbS/CdS NCs with thin and giant shell (thin and giant NCs,

respectively) and sharp core/shell interface have been compared. Both the samples have a PL peak at around 690 nm; however pumping above the CdS bandgap we can observe a strong PL at 480 nm only in giant NCs. These two emissions can be uniquely assigned to the exciton recombination from the core and shell states, respectively. The analysis of PL spectra as a function of the average exciton occupancy  $\langle N \rangle$  per NC reveal the nature of the difference between the two samples. Increasing  $\langle N \rangle$  in thin NCs the two emissions follow a common trend, while in giant NCs they appear dissociated ascribed to an exciton decoupling. We have studied the electron-hole distribution by DT measurements to investigate this dual emission mechanism. DT analysis of giant NCs allowed the detection of two different photobleaching



1. PL spectrum and sketches of the morphology and the energy structure of PbS/CdS NCs with giant shell.

(PB) signals assigned to the wurtzite (Wz) and zincblende (Zb) phases of the CdS shell, and the electron delocalization along the conduction band of the heterostructure pumping below the CdS bandgap, signature of the quasi-type II band alignment between the core and shell energy levels (Fig.1).

The temporal and spectral study of these PBs at different  $\langle N \rangle$  reveals the Auger recombination suppression and a clear increase of the exciton population in Wz CdS states related to the core state saturation.

These results attest that the efficient double emission process in giant NCs is due to a decoupling between core and shell excitons assisted by the large shell volume and the presence of a Zb-CdS barrier.

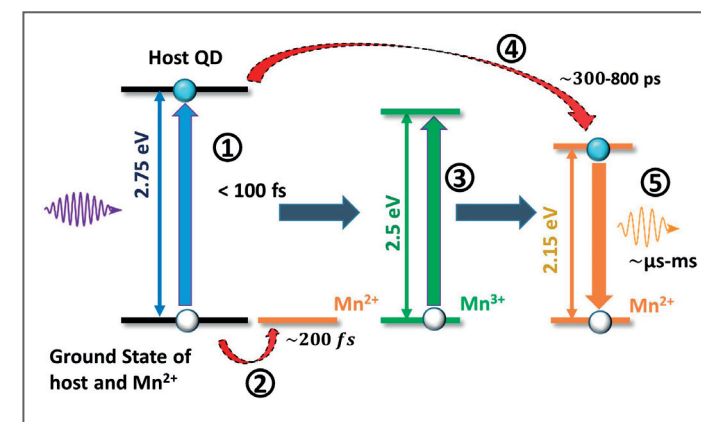
In addition, the deposition of giant NCs in film allows the achievement of amplified spontaneous emission (ASE) from the shell making them good candidates for lasing.

In order to study the effect of the shell structural composition in giant NCs two batches of CdSe/CdS NCs have been grown with the same core and shell dimensions and same sharp interface but with different CdS shell structure. In one case the CdS shell is uniquely composed by the Wz CdS phase (W/W NCs), while in the other case the CdS shell includes both the Zb and Wz CdS phases (Z/W NCs).

Both the samples show dual emission from the core and the shell and the achievement of ASE from the shell pumping by fs pulses. The comparison with

another similar sample with alloyed interface which exhibits single PL demonstrates that even only an abrupt core/shell interface allows the dual emission mechanism. Nonetheless these samples show profound differences in the hole relaxation from the shell to the core. PL and DT measurements reveal that while for  $\langle N \rangle < 1$  both samples show the same slow hole relaxation in the core, increasing

the excitation of  $Mn^{2+}$  is a spin forbidden transition and its mechanism is still not clear. By DT analysis we have discovered that the excitation of  $Mn^{2+}$  is a two-step mechanism (Fig.2) in which a hole is transferred from the NC to the  $Mn^{2+}$  which is converted in transient  $Mn^{3+}$  with spin-allowed transition at around 2.5 eV. This Mn species is excited by energy transfer from the host and converted again in  $Mn^{2+}$  accepting



2. Sketch of the two-step process that leads to  $Mn^{2+}$  emission

$\langle N \rangle$  this latter slows down just in Z/W NCs. At large  $\langle N \rangle$  The interfacial layer of Zb CdS in Z/W NCs creates a potential barrier in valence band that, together with the Coulomb repulsion leads to a dynamic hole blockade process which limits the core occupancy to just one hole. This barrier, present only in Z/W NCs, leads to the achievement of ASE also pumping ns pulses. Dual emission can be also achieved in Mn-doped CdZnSe NCs. The dual emission can be assigned to the recombination from the NC band-edge and from  $Mn^{2+}$  at 2.15 eV. Nevertheless,

electrons from the NC and finally can emit. These results allow a large understanding of the phenomena underlying the double emission process in different NCs and pave the way for their engineering in opto-electronic applications.

# ELUCIDATING THE ROLE OF INTERFACES AND INTERFACIAL LAYERS IN MIXED HALIDE PEROVSKITE SEMI-CONDUCTING DEVICES

Venugopalan Vijay – Supervisor: Dr. Annamaria Petrozza

Organic-Inorganic Mixed halide perovskites are crystalline direct band-gap semi-conductors, and interestingly they are 'soft' and easily deformed by applied fields and light. This gives rise to a rich variety of phenomena that occur in these semiconductors, wherein standard solid state physics dynamics change in time. Since Perovskites are ionic crystals their transformation in severe in the presence of electric field and light. What has been established in the last few years is that ions in the crystals have low activation energies to form interstitials and vacancies in the application of bias. Hence there is a motion of ions within the crystal within devices that contain a built-in potential or devices wherein fields are applied. Over the last couple of years it has been noticed that the interface of perovskite devices play a very important role in achieving highly efficient and stable devices. It has not been very clear, the role of interfacial layers in devices, the intrinsic changes in perovskite surfaces, the interaction of the perovskites with atmospheric oxygen/water vapour and related. Towards this end I have investigated my research in my PhD thesis. The research has been carried out at the Center for Nanoscience and Technology (CNST), Istituto

Italiano Di Tecnologia and the ARCO lab of Politecnico as a part of the physics department of Politecnico di Milano (Milan, Italy). Collaborations were started with the PoliFab lab of Politecnico Di Milano. Two secondments were performed with a) Prof. Juan Bisquert, University of Jaume, Castellon Spain and b) Prof. Henry Snaith, Clarendon Laboratory, University of Oxford.

The essence of the thesis can be broken into two parts:

- 1) Understanding the role of accumulating ions in MAPbI<sub>3</sub> solar cells and devices
- 2) Utilizing the learnt lessons and applying them to passivate interfaces for fabricating efficient opto-electronic devices

The Work is summarized below in Scientific Chronology:

## Interfacial Electronic Charge Accumulation and Trapped Charges in Perovskite Solar Cells:

It is widely assumed that many interfacial characteristics observed in MAPbI<sub>3</sub> solar cells arise due to the accumulated ions at the interface. Large capacitances are observed in the dark in the interface, heavy charge recombination is seen to originate from the interface, hysteresis is

again interface specific in these cells. All these characteristics until now were presumed to be due to the accumulation and diffusion of ions. However we show in this chapter that all these characteristics are caused by electronic charges and not ionic charges as previously assumed. Though the role of ions cannot be ruled out, what we show is that large charge accumulation of charges observed is of either electrons or holes; and that ionic accumulation is only a small contribution to the total accumulated charge.

## Investigating the Role of PCBM in Perovskite Solar Cells

PCBM is a C60-fullerene based n-type semiconductor that is heavily utilized in perovskite solar cells. It is known to suppress hysteresis and passivate trap states at the interface. Here we detail the mechanism of the reason why PCBM works so effectively – and why it is so unique in passivating the perovskite interface. We find that with PCBM there are no large charge accumulation at the interface, no hysteresis and large surface recombination of electronic charges. We find that ions that accumulate at the perovskite interface, specifically

Iodide ions, interact and dope the PCBM in a solid state reaction. Hence the hole-trap states created by the accumulated iodide ions are passivated by PCBM which acts as a 'dopable' interfacial layer. This gives a complete picture of the interface effects in MAPbI<sub>3</sub> solar cells: Iodide ions diffuse to the outer surface due to the in-built field and create large densities of hole traps at this interface. Since these are defect-states with a single interfacial defect capable of accumulating multiple holes, we obtain a large hole population at this interface. However if we apply an interfacial layer that can react chemically with the accumulated ions, these defect states can be passivated. – Hence a new strategy of dopable interfacial layers to stabilize the working of MAPbI<sub>3</sub> perovskites is put forth.

## Efficient MAPbI<sub>3</sub> Photoconductors through selective hole conduction:

In this chapter. We utilize PCBM to passivate the interface of printed perovskites and then demonstrate their performance as state of the art Photoconductors. We use all the properties of PCBM detailed earlier and successfully suppress the noise in the printed perovskites. This also leads to larger Responsivities and Specific

Detectivities. We show that we achieve such a performance due to a selective hole conduction in the perovskite. By using appropriate high work-function electrodes we circulate holes in the devices while the electron is transferred to PCBM, which leads to large gains in our devices.

## Enhancing Interfaces for MAPbI<sub>3</sub> devices : Layered Materials and Defect Passivation

In this chapter : I have major collaborations with my colleagues. In the first part WS<sub>2</sub> is utilized as a hole transport materials contacting the interface of the perovskite for broadband photodetectors. We find that this appreciably suppresses the noise in this device in comparison with the reference of Spiro-OMeTAD which is the interfacial layer that is always used. We find this to be an interfacial effect. Using WS<sub>2</sub> also markedly is expected to improve the stability of these photodetectors. In the second part of the chapter, with collaboration from the Chemistry Department of Politecnico Di Milano: we utilize passivants that can bind with the vacancies in perovskites in solar cells. We find that using selective binding groups is important for the chemical molecules to bind

with the defects in perovskites. This leads to an improvement of solar cells performances. Hence as a conclusion we show the importance of interfacial energetics in a direct band-gap ionic semiconductor in light of ionic accumulation at the interface. As a part of future work, I conclude by developing a new technique to measure recombination and transport lifetime specially for these class of solar cells which will be pursued further.

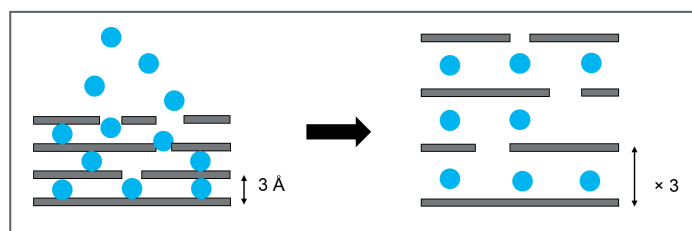
This PhD dissertation was funded by the European Union Initial Training Network : DESTINY (Dye Sensitized Solar Cells with Enhanced Stability). The author is a Marie Curie fellow early stage research fellow funded by DESTINY. The author takes opportunity to express his gratitude to his supervisor, tutor for their effective guidance and the European Union for its role and support.

# ANION INTERCALATION IN GRAPHITE: A COMBINED ELECTROCHEMICAL AFM AND STM INVESTIGATION

Yivlialin Rossella – Supervisor: Dr. Gianlorenzo Bussetti

Graphite electrodes have been, and continue to, be used widely in electrochemistry for a wide range of applications from energy conversion or storage (e.g. lithium-ion batteries and fuel cells) to electronic analysis (e.g. DNA analysis by carbon electronic chips) and in a wide range of sizes, from micron or submicron to electrodes with extension of square meters. Electrochemistry has been connected to graphite since the early days of its research activity because of its good electrical and thermal conductivity, corrosion resistance, low thermal expansion, low elasticity and high purity. The more traditional form of graphite implemented as electrode is the Highly Oriented Pyrolytic Graphite (HOPG) crystal. Nowadays, HOPG has also focused an additional increasing interest due to its layered structure, which can be thought in terms of a graphene sheets pile. In view of industrial implementation, we are obliged to combine a quantity and quality enhancement of graphene together with a cost production reduction. In these perspectives, electrochemical strategies are successful. Graphite is delaminated by anion intercalation inside the crystal at specific electrochemical potentials. Anions are placed in the inter-layer region and they expand the graphite

structure of about a factor of 3. Consequently, the layer-layer interaction is reduced and a gentle sonication dissolves part of the original HOPG crystal inside a suspension of graphene sheets. **Figure 1** summarizes this picture. Here, anions belong to a sulfuric acid water-based electrolyte. Despite good results are reported



**1. Sketchon the anion intercalation in graphite and the consequent expansion of the interlayer space**

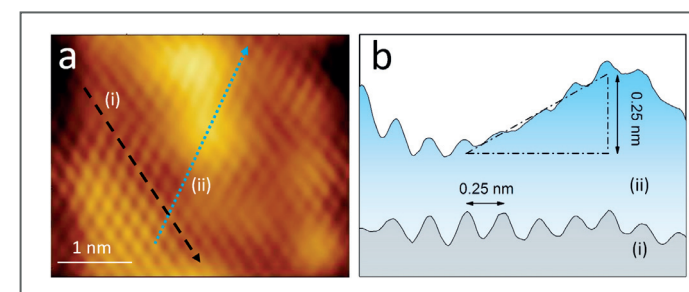
and discussed in the literature, the graphene sheet sizes are wide dispersed over a range of 2 order of magnitudes (radii from tens of nanometers up to 1 micrometer are observed). In addition, structural damages, defects, water and electrolyte contaminations are frequently reported. Most of the works follow a trial-and-error method but it has been recently noted that there is an unjustified lack of knowledges regarding the molecular mechanisms involved during anion intercalation in graphite. An explanation of the HOPG delamination steps can help

in a further optimization of the production protocol. This PhD thesis exploits an electrochemical scanning probe microscopy (EC-SPM) to disclose the first stages of sulfuric intercalation in graphite. The EC-SPM combines a traditional three-electrode cell with both an atomic force and scanning

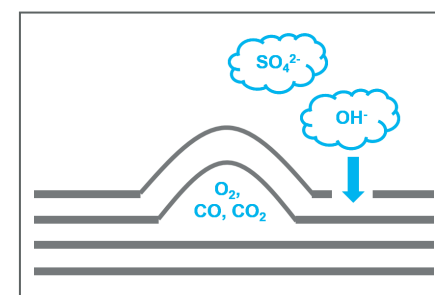
tunneling microscopy (AFM and STM, respectively) and is able to characterizes the morphology and local structure of the electrode surface as a function of the EC potential *in-situ* and in real time (during the EC potential changes). A traditional cyclic-voltammetry (CV), where the sample EC potential is ramped linearly versus time and the flowing current accordingly measured, allows a characterization of the electrolyte and ensures that EC processes occur at the graphite electrode surface. In this research, we proved

that the graphite basal plane is damaged when high anodic potentials are selected for the sample electrode. A carbon dissolution erodes graphite step edges or produces deep holes on surfaces. These processes are a clear detriment in view of graphene production, because the sheets show defects even

graphite surface and stretches the C-C bonds of few percent, promoting other structural lacerations. **Figure 2a** reports a typical blister as observed *in-situ* after anion intercalation. Panel b compares the atom periodicity along and across a blister to enhance the C-C bond stretch. Other typical electrolyte



**2. a) EC-STM topography of a blister after anion intercalation. b) Profiles across (dashed blue line) and along (dashed black line) the blister**



**3. Sketch of the interpretative model for the creation of blister. The intercalation of the sulfuric and OH<sup>-</sup> anions produce gases, swelling the graphite surface**

before the graphite delamination. In addition, the HOPG electrode is affected by blisters as soon as the oxygen overpotential is reached during the CV. Blisters swell the

used for intercalation (e.g. perchloric acid) show surface blistering. Blister evolution seems to be related to the oxidation of solvated anions and to a

subsequent evolution of gases (namely CO, CO<sub>2</sub> and O<sub>2</sub>). The compared analysis, driven at different EC potential, allows the definition of a new intercalation model, proposed in this thesis and illustrated in **Figure 3**. When the oxygen overpotential is reached during the CV, OH<sup>-</sup> anions penetrate inside HOPG and exchange an electron charge at the electrode-electrolyte interface. Oxygen is produced and the graphite surface partially swells. A further increase in the EC potential favors the sulfuric anion intercalation and a concomitant dissolution of carbon. CO and CO<sub>2</sub> are produced and wide areas of HOPG are affected by blisters. We believe that our findings shine a first light on the molecular mechanism involved during anion intercalation, helping technology to optimize the graphene production protocols. In particular, intercalation must be obtained with concentrated acids to avoid a percolation of solvated anions that favor the blister evolution. On the other hand, hydroxyl group intercalation is enough to swell graphite and helping the graphite delamination. We observe that this process occur before the anion intercalation limiting the crystal detriment due to graphite dissolution.

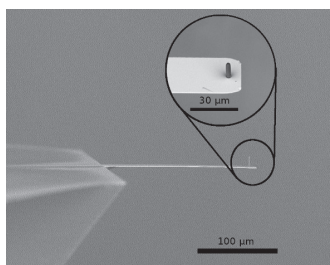
# THREE-DIMENSIONAL DIRECT WRITING OF MECHANICAL AND BIOMEDICAL MICRODEVICES BY TWO-PHOTON POLYMERIZATION

**Zandrini Tommaso – Supervisor: Dr. Roberto Osellame**

Two-photon polymerization (2PP) is an additive manufacturing technique that bridges the simplicity, versatility, and low cost of macroscopic 3D printing techniques, with the high resolution typical of conventional microfabrication techniques. It is based on the irradiation of the volume to be polymerized inside a UV sensitive photoresist through an infrared femtosecond laser, that will trigger polymerization only in its focus, without light absorption in the rest of the material.

This technique is able to realize small polymeric objects with a minimum feature size smaller than the light diffraction limit: the huge number and variety of photostructurable polymers available nowadays makes the applications of this technique virtually unlimited. Since its introduction in 1997, many advances have been realized by researchers worldwide: they explored many materials, increased the fabrication resolution, enhanced the process speed, and applied various techniques to add further functionalities to the microstructured polymeric parts. 2PP has been employed to produce both fixed and movable parts for Lab-on-a-chips, various micromechanical objects,

different classes of optical elements, arbitrarily shaped photonic crystals, and scaffolds for cell culture. In my thesis I have reported about the research projects I have been involved in, during the three years of PhD, about femtosecond laser fabrications, mainly with the technique of 2PP.



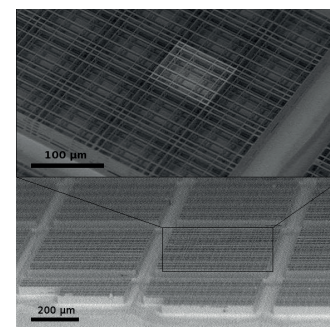
**1. Hydrophobic AFM tip for nanoindentation on soft hydrophilic samples, realized on top of a commercial tipless cantilever. The inset shows a detail of the tip**

To provide a powerful tool to perform nanoindentation measurements on soft hydrophilic samples, such as cell, proteins, hydrogels, and other biologically relevant samples, we produced atomic force microscopy (AFM) tips employing a highly hydrophobic photoresist, in collaboration with the Chemistry, Materials and Chemical Engineering

Department of Politecnico di Milano. Nanoindentation is a measure of the mechanical properties of a sample, performed in a very localized spot, allowing to test microscopic objects; an AFM tip is lowered towards the sample, and the deflection of the cantilever is monitored: attractive and adhesive forces between tip and sample can spoil the measurement, thus it is necessary to reduce them as much as possible. To achieve this result, we first tested several fluorinated photoresists to assess their compatibility with the 2PP process. Our experiments revealed that, among the ones tested, the only one photostructurable with 2PP exhibiting a very high contact angle with water was a PFPE-based material developed specifically for this task by our collaborators, which had a higher number of photoreactive functionalities than its commercial counterparts. With this material, we could fabricate a cylindrical tip, with a hemisphere con top, on a commercial tipless cantilever (Figure 1), that we validated with nanoindentation measurements of PDMS and PEGDA hydrogel. The expected elastic behaviour of PDMS was observed, confirming the good performances and stability of our tip. Measurements

on hydrogel were also successfully performed, showing how the PFPE tip is suitable for nanoindentation on highly hydrophilic samples. Both measurements exhibited lower attraction force and higher indentation range, which means higher quality data, than the ones obtained with a commercial nanoindentation tip functionalized in laboratory with a hydrophobic coating.

In the framework of a study on the effects of the mechanical stimuli provided to stem cells from their surrounding microenvironment, coordinated by the Mechanobiology Lab of Politecnico di Milano, we



**2. Scaffolds for stem cells cultivation and pluripotency maintenance. The single nichoid unit is highlighted in the top picture, showing a single block of 5x5 nichoids. A detail of a 3 mm radius circle covered by nichoid blocks is visible in the bottom picture**

fabricated cellular scaffolds with a biocompatible hybrid organic-inorganic photoresist, SZ2080. In particular, our aim was to inhibit the differentiation of stem cells, providing a network of ordered pillars and grids that

generates isotropic forces on the cytoskeleton and nucleus of the cells, mimicking the mechanical effect of the staminal niches in which they are naturally grown. To do so, we used an elementary structure that we called “nichoid”, able to confine cells inside its volume thanks to external walls, and constituted by three grids at ground, intermediate, and top level, with vertical columns at each grid intersection point. To obtain a considerable number of cultured cells, necessary to extract statistically relevant biological results, we started scaling up the fabrication process, passing from the three nichoids of the early works, to hundreds of them on the same sample, and finally to supermatrices composed by several nichoids with side walls in common (Figure 2). To do so, we employed a high speed translation system greatly increasing the fabrication velocity, we finely optimized the laser parameters to achieve mechanically stable structures, compensated for the substrate flatness over a large area, and tried to remove all the causes of instability and drifts of our fabrication setup, which are normally irrelevant over a few hours, but become problematic when the fabrications take half a day or more. The biological tests on our samples, performed in subsequent studies with human mesenchymal stem cells and murine embryonic stem cells, showed that pluripotency is maintained more in our scaffolds than on flat glass or on another three-dimensional biological matrix, showing a higher count of staminality markers and a

lower one of differentiation markers towards different cellular lineages. The studies will continue to determine with more precision the causes that produce this behaviour.

Since polymeric 2PP structures are limited in functionalities, several techniques are used to provide additional chemical and physical properties. Electroless plating is one of these techniques, and during my stay at Yokohama National University, I had the opportunity to use it to magnetize microrotors made out of an acrylic resin, for microfluidics applications. We performed magnetite electroless plating, to make the rotors ferromagnetic, and realized the shafts with a methacrylic polymer, refractory to electroless plating, exploiting the selectivity of this technique, to reduce friction and attraction between the two parts. We demonstrated smooth rotation of our devices immersed in a solution of water and the surfactant Triton X-100, using a magnetic stirrer. We could obtain simultaneous rotation of several rotors, at speeds between 200 and 600 rpm, as set in the stirrer. These devices could be inserted in microchannels to control the flow inside them, or to mix separate laminar flows.