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Corrado Spinella (Dipartimento di Scienze Fisiche e Tecnologie della Materia - CNR)

Maurizio Peruzzini (Dipartimento di Scienze Chimiche e Tecnologie dei Materiali - CNR)

Italian National Conference on
Materials Science and Technology
Bologna, October 22 - 26, 2018

Conference Chairs

Corrado Spinella (DSFTM - CNR)

Maurizio Peruzzini (DSCTM - CNR)

BOOK OF ABSTRACT



SPRINGER NATURE



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Plenary sessions

Monday, October 22

- 12:00 -13:00 **Andreas Züttel** EPFL Lausanne (Switzerland)
Energy storage materials, hydrogen storage materials
- 14:00 -15:00 **Avelino Corma** CSIC (Spain)
Attempts to synthesize zeolite catalysts for a preselected reaction

Tuesday, October 23

- 09:00 -10:00 **Nicolas Giuseppone** CNRS Strasbourg (France)
Stimuli-responsive materials for mechanical actuation
- 16:30 -17:30 **Giovanni Baldi** CE.RI.COL Colorobbia Research Centre (Italy)
Hybrid magnetic-polymeric nanoparticles for nano medicine and immune therapy

Wednesday, October 24

- 09:00-10:00 **Gaetano Granozzi** Università di Padova (Italy)
3D Hybrid nanoarchitectures for sustainable energetics starting from 2d materials
- 16:30 -17:30 **Salvo Coffa** STMICROELECTRONICS (Italy)
Materials for the electronic industry

Thursday, October 25

- 09:00-10:00 **Miriam Vitiello** CNR - NANO (Italy)
Title to be defined
- 16:30 -17:30 **Luisa De Cola** Université de Strasbourg (France)
Self-assembled and breakable materials for medical applications



Renewable Energy Storage in Hydrides and Hydrocarbons

Prof. Dr. Andreas ZÜTTEL

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The first publication of the global warming due to the increase of the CO₂ concentration in the atmosphere by Svante Arrhenius in 1896 in the Philosophical Magazine was doubted and ignored for almost 100 years. Only at the end of the last century the global consequences of the anthropic CO₂ emission became a major concern and science and technology focused on the conversion of renewable energy (solar, wind, hydro) in order to reduce the dependency on fossil fuels and reduce the emission of CO₂. However, the recent development in installed peak power of wind generators and photovoltaics clearly indicates that storage of energy from renewable sources is the greatest challenge of the coming 10 years. Thereby the production of fuels for mobility and the long term (seasonal storage) of renewable energy are the key technologies, because mobility requires a high gravimetric and volumetric energy density (10 kWh·kg⁻¹, 10 MWh·m⁻³) and the storage of large amounts of energy requires an economic energy carrier like fossil oil (few cents per kWh). The technical solution is to produce hydrogen from renewable electricity. Hydrogen production by electrolysis is an established technology also currently we are facing a lack of large scale electrolyzers available. The storage of hydrogen under high pressure, in liquid form or in hydrides is a material challenge and limited to 50% of the energy density of liquid hydrocarbons. The hydrogen can be used to reduce CO₂ from the atmosphere in order to synthesize liquid hydrocarbons. This requires large scale electrolyzers, hydrogen storage, adsorption of CO₂ and finally a well controlled reaction of H₂ and CO₂ to a specific product, e.g. octane. The storage of liquid hydrocarbons is an established technology.

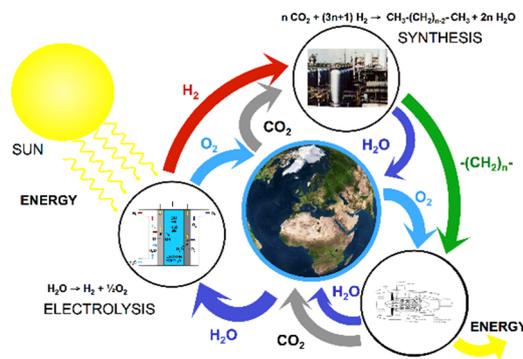


Fig. Schematic representation of the closed materials cycle, where hydrogen is produced from renewable energy and used together with CO₂ from the atmosphere to synthesize hydrocarbons as CO₂ neutral energy carriers.

Hugh progress was made in the development of new hydrogen storage systems in the last 20 years and the gravimetric hydrogen density was increased by an order of magnitude in hydrides. However, based on today's physical and chemical knowledge we will not be able to double the hydrogen density in materials anymore. The only solution in order to provide the energy density comparable to fossil fuels at a low cost is to close the carbon cycle and to develop chemical and electrochemical processes in order to synthesize liquid hydrocarbons from renewable electricity, hydrogen and CO₂ from the atmosphere.

Attempts to synthesize zeolite catalysts for a preselected reaction

by

Prof. Avelino Corma

Instituto de Tecnología Química

Different zeolite synthesis concepts have resulted in a better understanding of the synthesis mechanisms and in the development of new structures and applications. From the point of view of the zeolitic catalysts, previous knowledge and intuition allows to select, among different structures, those that may be useful to catalyse a certain reaction. The main criteria of selection is based on pore dimensions and pore topology. Then, when a first selection has been made, further improvements can be achieved by adapting chemical composition and crystallite size.

There is no doubt that it would be desirable to directly synthesize a zeolite that fulfils the geometrical requirements for a given reaction, while locating the active sites at the required framework position, in such a way that an optimum matching between the zeolite and the reaction transition state will be established. This should drive into a minimization of the activation energy of the process and, specially, a maximization of the selectivity to the desired product.

Besides discussing synthesis methods for preparing new zeolites, based on former concepts, and showing their possibilities for adsorption/separation and catalysis, a methodology for the “*a priori*” synthesis of zeolites directed to specific applications will be presented. Within this methodology, a reaction mechanism for the catalytic process is first postulated, that includes a potential reaction transition state. Then, a mimic of such a transition states (TS) is synthesized as Organic Structure Directing Agent (OSDA) and the zeolite synthesis is carried out certainly using previous existing knowledge on the influence of gel composition time and temperature, for performing the synthesis. The methodology not only should be useful for directing into structures with pores and cavities adapted for reaction TS stabilization, but also should direct the location of framework charge compensation for a given catalytic reaction.

It will be shown that, following the above methodology, it is possible to prepare zeolites with improved activity and selectivity than the ones used today for chemical and petrochemical processes during alkylaromatics transformations, and for cracking processes directed to maximize olefins productions.

Integration of Molecular Machines in Active Polymer Materials

Prof. Nicolas Giuseppone

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Abstract: Making molecular machines that can be useful in the macroscopic world is a challenging long-term goal of nanoscience. Inspired by the protein machinery found in biological systems, and based on the theoretical understanding of the physics of motion at the nanoscale, organic chemists have developed a number of molecules that can produce work when triggered by various external chemical or physical stimuli. In particular, basic molecular switches that commute between at least two thermodynamic minima and more advanced molecular motors that behave as dissipative units working far from equilibrium when fueled with external energy have been reported. However, the ultimate challenge of coordinating individual molecular motors in a continuous mechanical process that can have a measurable effect at the macroscale has remained elusive until very recently. We will discuss advances developed by our group on artificial molecular machines and involving their mechanical coupling within dynamic polymer systems. We will show that it is now possible to amplify their individual motions to achieve macroscopic functions in materials. In particular, we will present a dual-light controlled system operating fully out-of-equilibrium, and in which the integrated motions of two types of mechanically active units can be tuned by modulation of frequencies.

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Hybrid magnetic-polymeric nanoparticles for nano medicine and immune therapy

A platform based on a Nano Carrier system to be employed as a theranostic tool for the treatment of cancer and/or aging-associated neurodegenerative diseases is presented. The theranostic approach (therapy and diagnosis) takes advantage of the possibility to employ nanostructured materials simultaneously as multifunctional platforms for hyperthermic treatment, controlled drug release and imaging/sensing applications.

A multifunctional system based on a hybrid inorganic(magnetic)/organic nano-carrier, superficially decorated with specific targeting moieties (monoclonal antibodies and/or protein-based units for cellular recognition) and loaded with specific anticancer drugs was customized for treatment of pancreatic and head-neck cancer. Preliminary results are presented in this speech.

Recently an other approach has been developed for melanoma and multiple sclerosis :a robust technique to load hybrid nanoparticles into T-lymphocytes still maintaining their viability and functionality unaffected. T-cells were chosen because they can be selected and multiplied to strengthen their cytotoxicity towards tumoral cells and the possibility to mediate the inflammatory processes in the brain. This method implies the preparation of products based on live-cells with the aim of enhancing their therapeutic, diagnostic or preventive effect.

HYBRID NANOARCHITECTURES FOR SUSTAINABLE ENERGETICS STARTING FROM 2D MATERIALS

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Graphene (G) and other 2D materials (e.g. h-BN, layered chalcogenides, carbides, and oxides) are altogether referred as Graphene Related Materials (GRMs) and they are gaining a great interest for their exceptional properties. Nowadays, the forefront of research has progressed from the simple GRMs preparation and characterization toward their use in real applications. Whereas in some devices (photonics, optoelectronics...) the goal is the most perfect GRMs assemblies with defectless interfaces, in the case of catalysts (either photo- and electro- and thermal catalysts) and sensors, the quantity and quality of the exposed surfaces and their defectivity play a leading role for the designed functionalities. In these cases, chemically-modified high surface area GRMs hybrid nanoarchitectures (organized in 2D and 3D) are the target.

The Surface Science and Catalysis group (SSCG) of the University of Padova¹ is strongly committed in exploiting the innovative properties of GRMs materials to be used as photo-, electro- and photoelectrocatalysts for the development of sustainable energetics. Among others, one route we are currently exploring is to covalently functionalize the 2D materials with electroactive molecules to develop new properties that the pristine materials do not possess in order to broaden their application in catalysis and sensing. Actually, while covalent functionalization of carbon nanostructures (graphene, nanotubes, etc) is much developed,² a similar approach for other 2D materials is still at its infancy.³ In this lecture the most significant outcomes obtained in the SSCG will be outlined discussing recent examples of electrocatalysts for the Oxygen Reduction Reaction (ORR), Hydrogen Evolution Reaction (HER) and Carbon Dioxide Reduction Reaction (CRR).

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¹ People of the SSCG currently involved in the present topic are: Stefano Agnoli, Laura Calvillo, Matias Blanco, Dario Mosconi.

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³ S. Presolski and M. Pumera, *Materials Today*, 19, 2016, 3

Self-assembled and breakable materials for medical applications

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Despite the substantial progress that has been made in biomaterials synthesis and functionalization, the challenge of delivery in vivo in desired organs biomolecules or drugs and to mimic the ECM with implants that are able to reduce immunoresponse is still unmet.

Towards this aim, we reported a novel biocompatible hydrogel with the ability to release a migration-inducing factor, for the recruitment of stem cells [1]. The hydrogel is a composite made of breakable container –type materials able to respond to an external stimulus. In particular in the last 5 years we devoted much effort in the creation of “containers’ able to break in small fragments (<5 nm) by a redox reactions,[2] enzymatic degradation,[3] and pH. They can also be capsules in which large biomolecules such as enzymes and proteins can be entrapped and release on demand [4]. The hydrogels that contain such containers are formed in physiological conditions, without any catalyst and at room or at body temperature. They are perfectly biocompatible and can be made degradable. Cells are able to populate and proliferate in the matrices and even stem cells are able to grow and differentiate. Interestingly these soft materials can be injected as liquid and are able to solidify in few seconds or even in milliseconds in different tissues and organs.

Finally I wish to close my talk showing novel capsules that can be realized using a unique approach to template virus proteins to reconstruct virus-like particles. We use luminescent Pt(II)-complex amphiphiles, able to form supramolecular structures in water solutions, [5] that can act as templates of viruses capsid proteins. The platinum assemblies can have different morphologies and extremely high emission of which the color depends on the assembly. Interestingly we are able to change the size and shape of the particles even though we use the same natural proteins. The obtained virus-like particles can be visualized by their intense emission at room temperature, generated by the self-assembly of the Pt(II)-complexes inside the capsid [6].

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Parallel sessions

Monday, October 22 15:00 - 17:00

Materials and Modelling for Energy Conversion
Colloidal particles and nanoparticles
Metamaterials, Plasmonics and Nanophotonic systems
Cultural Heritage

Monday, October 22 17:30- 19:30

Materials and Modelling for Energy Conversion
Photophysical and Non-linear Phenomena
Computational and experimental methods for soft matter

Tuesday, October 23 11:00 - 13:00

Materials and Processes for Environment Protection and Sustainability
Materials and Processes for Environment Protection and Sustainability
Molecular self-assembly and supramolecular materials
Organic/Hybrid and Printed Electronics and Photonics

Tuesday, October 23 14:00 - 16:00

Materials and Processing for Energy
Biomaterials for Regenerative Medicine
Molecular self-assembly and self-organized nano and mesostructures
2D Materials for Energy and Environmental Applications

Tuesday, October 23 17:30 - 19:30

Materials and Processing for Energy
Materials and Processes for Environment Protection and Sustainability
Biomaterials for Regenerative Medicine/Additive Manufacturing in Biomedical Research and Active Packing Materials

Wednesday, October 24 11:00 - 13:00

Growth and Synthesis of 2D Materials
Organic, polymer and hybrid nanostructures, and bio soft materials
Stimuli-responsive materials

Wednesday, October 24 14:00 - 16:00

Low-dimensional Structures for Nanoelectronics and Nanophotonics
Chemical Functionalization and Characterization of 2D Materials
Stimuli Responsive Bioorganic Materials and Smart Surfaces
Advanced Structural Characterization of 2D Materials

Thursday, October 25 11:00 - 13:00

Chemical Functionalization and Characterization of 2D Materials
Organic/Hybrid and Printed Electronics and Photonics
Nanobiocomposites for In-vitro Diagnostics and Targeted Drugs
Topology and Electronic Correlation in Magnetism and Superconductivity

Thursday, October 25 14:00 - 16:00

Advanced Nanofabrication and Characterization of Electronic and Photonic Devices
Organic/Hybrid and Printed Electronics and Photonics
Fundamental Physical Properties of 2D Materials and their Heterostructures
Metamaterials, Plasmonics and Nanophotonic systems

Thursday, October 25 16:30 - 18:30

Advanced Nanofabrication and Characterization of Electronic and Photonic Devices
Electronic and Photonic Devices for Biological Applications
First Principles Modelling of 2D Materials and their Heterostructures

Friday, October 26 10:00 - 12:00

Organic/Hybrid and Printed Electronics and Photonics
Low-dimensional Structures for Nanoelectronics and Nanophotonics
Advanced Spintronics and Nanomagnetism: Materials and Devices
Materials and Technologies for Energy Storage

Materials and Modelling for Energy Conversion	Francesca Passaretti
Colloidal particles and nanoparticles	Andrea Camposeo
Metamaterials, Plasmonics and Nanophotonic systems	Adriana Passaseo
Cultural Heritage	Alessandra Sanson
Materials and Modelling for Energy Conversion	Federico Boscherini
Photophysical and Non-linear Phenomena	Giampiero Ruani
Computational and experimental methods for soft matter	Andrea Camposeo

#001 - Thermoelectric properties of fast sintered polycrystalline SnSe composites

Carlo Fanciulli - CNR - ICMATE

Other Authors: Stefano Boldrini (CNR - ICMATE, Corso Stati Uniti 4, Padova), Alberto Ferrario (CNR - ICMATE, Corso Stati Uniti 4, Padova), Corrado Tomasi (CNR - ICMATE, Via De Marinis 6, Genova), Hossein Abedi (CNR - ICMATE, Via Previati 1, Lecco), Francesca Passaretti (CNR - ICMATE, Via Previati 1, Lecco)

Tin selenide recently came to the research community interest due to the high performances observed in single crystals. Despite the high ZT of the material, the need to improve the mechanical behavior of the material suggested to move to the polycrystalline form trying to achieve a material easily workable preserving the thermoelectric characteristics of the material. However, the results reported for the polycrystalline SnSe compound are generally far from the expected ones. The characteristic mainly affected by passing to polycrystalline phase, considering the data reported in literature, seems to be the electrical conductivity. In fact, it not only scales due to the new microstructure, but it also changes in temperature behavior. At the same time the ultra-low thermal conductivity is not improved by the presence of phonon scattering introduced by the polycrystalline microstructure.

In this work, composites have been produced starting from SnSe powders sintered using open die pressing technique. Metallic particles have been added to improve the carrier mobility into the system trying to achieve a conductivity behavior closer to the best one reported in literature. In particular, experiments adding boron and copper have been performed. Preliminary results on the structural effects of the composition and on thermoelectric properties are reported.

#002 - Investigation of microstructural and functional properties of polycrystalline samples of NiMnGaCu ferromagnetic shape memory alloy

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In the last 20 years Magnetic Shape Memory Alloys (MSMA) attracted increasing attention for their different properties and smart functions. Starting from the first and most important system NiMnGa, a long series of quaternary alloys was developed to improve the performance of these materials in the Giant Magnetostrictive Effect (or Magnetic Field Induction Strain), Magnetic Shape Memory effect, Magnetocaloric and Magnetoresistive properties and also Elastocaloric response. Some alloys like NiMnInCo, NiMnSn or NiMnGaCo showed interesting giant magnetocaloric effect using the superimposition in temperature of magnetic transition and thermoelastic martensitic transformation; in this way under magnetic field the resulting entropy variation (DS) is maximized by the overlapping of these two physical transitions in the material. Therefore, these alloys open new perspective in the development of devices for magnetic solid state refrigeration. In the last years NiMnGaCu showed interesting magnetocaloric properties and the Ni₅₀Mn_{18.5}Cu_{6.5}Ga₂₅ (at%) alloys gives rise to the highest magnetic DS: -81.75 J/KgK at 302.5 K by magnetic field change of 9 T. This results that was obtained near room temperature is very important for the development of applications. In our work we prepared polycrystalline samples of the latter quaternary Ni₅₀Mn_{18.5}Cu_{6.5}Ga₂₅ alloy, where Cu is in substitution of Mn. By different kind of thermal treatments we modulated the microstructure of the alloy and we investigated the correlation between microstructural and functional properties. Magnetocaloric response was measured and a complete calorimetric and structural characterization was utilized to investigate this possible correlation. Moreover, to study the overcoming of brittleness problems, mechanical measurements completes the informations about the optimization of the material for future development of applications.

#003 - Organic semiconductors for printable thermoelectric applications

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Conductive polymers have attracted great attention for thermoelectric energy harvesting arising from easy processability, large availability, and intrinsically low thermal conductivity [1], since a large part of lost heat is at temperatures below 150 C [2].

In this work, different polymeric semiconductors are considered as interesting p-type thermoelectric materials. First, blade coating and slot die coating have been employed to deposit PEDOT:PSS as p-type polymer from two commercial formulations, namely Clevios PH1000 and Clevios FHC SOLAR. The experimental parameters of the two techniques have been carefully tuned to achieve thick and uniform PEDOT:PSS films on glass. Optical and structural characterization has been carried out to find the suitable properties of the two materials for thermoelectrics.

As-prepared PEDOT:PSS films solution show low thermoelectric properties, therefore a secondary doping is needed to enhance the electrical conductivity [3]. An easy protocol of doping treatment has been developed by immersing the coated PEDOT:PSS films into alcohols and basic solutions. Sheet resistance values of the films have been decreased to less than 10 Ω/sq, Seebeck coefficients up to 20 μVK⁻¹ and significant power factors of hundreds of μWm⁻¹ K⁻² have been achieved after doping treatment.

A second semiconductor investigated is poly(3-hexylthiophene) (P3HT), a promising semiconductor for thermoelectric application. P3HT has large Seebeck coefficient and is soluble in common organic solvents. However, it suffers from its low conductivity. Seebeck coefficient inversely scale to the conductivity and power factor is directly related to conductivity [4]. With increasing conductivity, the power factor will increase. It is therefore important to increase the conductance in P3HT layers. There were a lot effort to increase the conductivity of P3HT, like using different molecular configurations [5], using different solvents [4] tuning the additive [6]. In this work, we focus our attention on possible dopants such as iron salts, as ferric salt of triflimide anions [7], FeCl₃/nitromethane [8] or Iron(III) p-toluenesulfonate hexahydrate [9].

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#004 - Plasmonic metal nanoparticles as visible light photosensitizers for wide band-gap catalytic oxides

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The possibility to sensitize wide band gap oxides to visible light has stimulated the research community in view of efficiently converting solar to chemical energy, with the aim of obtaining optimized materials for photo-catalysis and sensor applications. As an alternative to titanium oxide, cerium oxide has been investigated due to the possibility for Ce ions to easily and reversibly switch between the 4+ and the 3+ oxidation states depending on the ambient conditions. In cerium oxide, the presence of localized Ce 4f states between the filled O 2p valence band and the empty Ce 5d conduction band can make the material a very sensitive probe to identify possible charge transfer to/from neighboring metal atoms. The occupation of the 4f levels is in turn expected to modify the material properties, decreasing the oxygen vacancy formation energy and modifying its optical response.

Pure CeO₂ absorbs light in the ultraviolet range (band gap 3.2 eV). To achieve a high efficiency for solar to chemical energy conversion, the material can be coupled with plasmonic nanoparticles (NPs). Irradiation with photon energies which excite the localized surface plasmon resonance (LSPR) can induce energy and/or charge transfer from the metal to the oxide, through a rich variety of mutual interactions, still largely unexplored in terms of the atomic scale description of the processes involved, though undoubtedly responsible for the enhancement of the activity of the material [1][2].

Cluster assembly in an inert gas condensation chamber combined with mass filtering allow us to obtain silver NPs with different LSPR excitation energies. These nanostructures were fully embedded in the CeO₂ matrix in order to maximize the interface area between the oxide and the metal and to prevent the oxidation of the NPs. Transient absorption spectroscopy (TAS) was used to explore mechanisms of energy/charge transfer at femtosecond/picosecond time scale in the Ag/CeO₂ systems.

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#005 - Synthesis of Nanometric Cerium Oxide-based Powders for catalytic and energetic applications

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Cerium oxide (CeO₂) has been extensively used in a wide range of applications and it has attracted extensive attention for its catalytic properties which were found to be size, shape and orientation-dependent. When doped with Gd, CeO₂ becomes an alternative electrolyte for Intermediate Temperature Solid Oxide Fuel Cells (IT-SOFC). Although several methods were proposed for the powders synthesis, most of them generally require a subsequent calcination step. This treatment is known to promote the crystallization of the amorphous phase, inducing aggregation and reducing the specific surface area (SSA) of the powder. In this work ultrafine CeO₂ and Gd-doped CeO₂ powders were obtained using standard chemical routes coupled with non-conventional heating processes. The correlation of the synthesis parameters with the thermodynamic and kinetic factors involved, allowed the control of properties such as size distribution, purity and morphology. Nano-structured ceria with complex morphology and high SSA was prepared by adjusting the synthesis conditions. These mesoporous aggregates were found to be active in the catalytic oxidation of toluene. The GDC obtained through the optimization of the synthesis parameters exhibited high values of ionic conductivity suitable for IT-SOFC applications.

#006 - The Ag - CeO₂ system: reducibility and interaction with H₂

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Cerium oxide in combination with supported metal nanoparticles or with dopants is one of the most important industrial and environmental catalysts. Its ability to reversibly form and fill oxygen vacancies, linked to the possibility to quickly change the oxidation state between 4⁺ and 3⁺, determines its activity in redox reactions. The combination of cerium oxide and metals is often beneficial, with the metal providing adsorption sites for reactants and the oxide releasing or storing oxygen ions. Moreover, the specific interaction between the two materials can sometimes lead to optimized properties, such as a higher reducibility or stability.

In previous works we studied the nature of the interaction between cerium oxide and metals using well-controlled model systems made of single crystalline epitaxial films combined with metals in different ways [1-4].

We report here an investigation of the interaction between Ag and CeO₂, pointing at substituting critical metals such as platinum, widely used as a catalyst for example in fuel cell electrodes. CeO₂ epitaxial films are grown by reactive molecular beam epitaxy. Ag is combined with CeO₂ in the form of size-controlled supported nanoparticles or substituted to a fraction of cerium ions in the oxide by co-evaporation. The reducibility of the system is studied during reduction and oxidation thermal cycles in vacuum and in oxygen background pressure. The results are compared with those obtained by reducing the system in H₂ background pressure. The modifications of cerium ions oxidation state are addressed by XPS, the structural modifications are evaluated by LEED, while the morphology is characterized using STM.

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#007 - Wall accumulation of bacteria with different motility patterns

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We systematically investigate the role of different swimming patterns on the concentration distribution of bacterial suspensions confined between two flat walls, by considering wild-type motility *Escherichia coli* and *Pseudomonas aeruginosa*, which perform Run and Tumble and Run and Reverse patterns, respectively. The experiments count motile bacteria at different distances from the bottom wall. In agreement with previous studies, an accumulation of motile bacteria close to the walls is observed. Different wall separations, ranging from 100 to 250 μm , are tested. The concentration profiles result to be independent on the motility pattern and on the walls' separation. These results are confirmed by numerical simulations, based on a collection of self-propelled dumbbells-like particles interacting only through steric interactions. The good agreement with the simulations suggests that the behavior of the investigated bacterial suspensions is determined mainly by steric collisions and self-propulsion, as well as hydrodynamic interactions.

#008 - Anisotropic Gold Nanoparticles: where shape becomes essence

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The topic concerns the synthesis and characterization of gold nanoparticles. The main goal of this topic is to emphasize the *correlation* between size, shape, and environment of nanoparticles and their plasmonic properties. As the shape or size of the nanoparticle changes, the surface geometry changes causing a shift in the electric field density on the surface. This causes a modification of the oscillation frequency of the electrons, generating different cross-sections for the optical properties including absorption and scattering. The refractive index of the surrounding medium (capping agent and solvent), as well as the average distance between neighboring metal nanoparticles, has been shown to influence the spectral features.

#009 - Plasmon-mediated cancer phototherapy: the combined effect of thermal and photodynamic processes

Loredana Ricciardi - CNR Nanotec-Institute of Nanotechnology

A nanoplatform for simultaneous cellular imaging, and photodynamic and photothermal therapies has been designed and realized by embedding a purposely synthesized highly luminescent water soluble iridium(III) compound into gold core-silica shell nanoparticles. These multifunctionalities arise mainly from the photophysical properties of the cyclometalated complex: (i) the heavy atom promotes, through excited triplet state formation, energy transfer processes towards molecular oxygen, with the generation of $^1\text{O}_2$ (photodynamic effect); (ii) the overlap of the iridium(III) complex emission band with the plasmonic resonance of gold nanostructures allows excitation energy transfer towards the metallic core (photothermal effect); (iii) the remarkable iridium(III) complex luminescence feature, which is preserved despite energy transfer processes, makes the whole system an efficient luminescent bio-probe (imaging). Photophysical and photothermal investigations have been carried out, whereas in vitro photo-cytotoxicity tests have been performed on human glioblastoma cells (U87MG), highlighting significant cancer cell death at a very low photosensitizer concentration ($<0.5 \mu\text{M}$), by means of a synergistic photodynamic and photothermal effect.

#010 - Surface Chemistry Impact on the Electronic Structure of Colloidal Quantum Dots

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Surface chemistry modification of as-synthesized colloidal semiconductor nanocrystals (QDs), commonly referred to as ligand exchange, is mandatory towards effective QD-based optoelectronic and photocatalytic applications. The widespread recourse to ligand exchange procedures is leading to uncover the marked impact exerted by surface chemistry on the QD optical properties: indeed, QD surface modification has been shown to induce, among others, optical band gap reduction[1] and broadband optical absorption enhancement[2], although little consensus exists on explanation of these experimental evidences. Here a comprehensive chalcogenol ligand library is exploited to describe and explain such phenomena. Indeed, surface chemistry does drastically modify the QD optical properties to an extent that almost linearly scales with surface-to-volume ratio as a result of the intrinsic ligand contribution to the overall QD electronic structure. As opposed to models based on the analogy with core/shell heterostructures that consider ligands as dielectric shell or potential energy barrier at the core boundaries, the indecomposable character of ligand/core adducts (the colloidal QDs themselves) arises.

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#011 - 3D to 2D reorganization of silver-thiol nanostructures, triggered by solvent vapor annealing

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Metal-organic composites are of great interest for a wide range of applications. The control of their structure remains a challenge, one of the problem being a complex interplay of covalent and supramolecular interactions. Herein we describe the self-assembly, thermal stability and phase transitions of ordered structures of silver atoms and thiol molecules spanning from molecular to mesoscopic scale. We used as ideal building blocks molecularly defined clusters formed by 44 silver atoms, each particle coated by a monolayer of 30 thiol ligands. By changing solvent and temperature, we could form 3D crystals of pristine nanoparticles or, conversely, 2D layered structures, with alternated stacks of Ag atoms and thiol monolayers. We studied the morphological, chemical and structural stability of these materials between 25 and 300 °C in-situ and ex-situ at the nanoscale by combining optical and electronic spectroscopic and scattering techniques, scanning probe microscopies and density-functional theory (DFT) calculations. The layered structure formed in this way showed a remarkable stability up to 200 °C.

#012 - Inversion of Wide Angle X-ray Total Scattering data for nanoparticle sizing and nano-structural characterization

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Nanoparticle sizing and structural characterization have become over the last decades topics of great increasing interest due to their intimate relationship to nanoscience and nanotechnology, with applications ranging from nanomedicine and nanobiomaterials, to nanoelectronics and energy devices production [1].

At the nanoscale (~1-100 nm), nanoparticles (NP) usually exhibit a crystalline or a partially ordered atomic arrangement, with local structural distortions, defects, and remarkable surface effects that can be tailored by properly manipulating the surface. All these features together with their morphology and Particle Size Distribution (PSD), determine the NPs physical-chemical properties and, ultimately, their functionality [2].

Recently, with the advent of methods called Wide Angle X-ray Total Scattering (WAXTS), the possibility of simultaneously characterizing the NPs structure and their PSD has become at hand within a single technique. The methods work by analyzing the total X-ray pattern scattered by the sample at wide angles and, by exploiting information from peaks positions, shape and width, can recover particle composition, structure, defects, morphology and size distribution.

One of the WAXTS techniques is based on the use of the Debye Scattering Equation (DSE) that describes the scattered intensity profile by randomly oriented polymorphic nanocrystals of different sizes and shapes, provided that all the distances between atomic pairs are known. Thus, by making the assumption that the PSD of each phase is described by a Log-Normal distribution, the WAXTS-DSE method recovers average, standard deviation, and concentration of each phase by standard χ^2 minimization. Clearly, when the assumption of a Log-Normal PSD is not appropriate, the WAXTS-DSE analysis becomes doubtful.

In this work, we remove the above limitation and propose, for the first time, the use of a non-linear iterative algorithm for inverting WAXTS-DSE data without imposing any constraints on PSD shapes [3]. Numerical simulations carried out on TiO₂ polymorphs and micro strained Fe₅Te₄ nanocrystals, show that the method, beyond being highly efficient and very robust against statistical noise, is also capable of recovering multi-peaked PSDs and pin down structural and morphological features of microstrains as well. Very promising results have also been obtained on real samples, which include superparamagnetic iron oxide NPs, N-doped nanoapatites and colloidal quantum dots.

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#013 - Molecular structure and multi-body interactions in polymer nanocomposites

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Polymer composites containing nanosized particles are currently the object of an intensive investigation, for the capability of these material to generate new potential technologies [1]. In this context, the stability of the resulting nanocomposite material is of primary importance, since the addition of nanosized fillers into the polymer matrix can significantly influence its overall behavior. In particular, the potential of mean force (PMF) between the nanoparticles embedded in the polymer is the most investigated issue when studying the stability of polymer nanocomposites [2].

Here we present a simulation study of the PMF in a coarse-grained model of silica nanoparticles merged in a polystyrene matrix by using the hybrid particle-field molecular dynamics approach [3]. In our study, nanoparticles are considered both ungrafted and grafted with further polystyrene chains. The resulting interactions are strongly attractive if the nanoparticles are ungrafted, becoming progressively more repulsive upon increasing the grafting density. A deeper insight into the microscopic mechanisms underlying the effective interactions is gained by calculating the three-body contribution to the PMF; in such a way it is possible to compare our results with previous simulation [4] and experimental [5] morphological diagrams, finding a good correspondence between the behavior of the PMF and various self-assembled phases. In particular, it emerges that the knowledge of three-body effects is crucial for identifying the nature of self-assembled nanostructures, like strings, connected sheets or small clusters.

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#014 - On the relevance of plasmon assisted generation of secondary electron*Alessandro Ruocco (I) - Dipartimento di Scienze, Università Roma Tre**Other Authors: Gianluca Di Filippo (Dipartimento di Scienze, Università Roma Tre, Rome Italy), Wolfgang. S.M. Werner (Institut für Angewandte Physik, Vienna University of Technology, Vienna, Austria), M.I. Trioni (CNR – ISTM, via Golgi 19, 20133 Milan, Italy), F. Offi (Dipartimento di Scienze, Università Roma Tre, Rome Italy), S. Iacubucci (CNR - ISM c/o Università Roma Tre, Rome Italy), G. Stefani (Dipartimento di Scienze, Università Roma Tre, Rome Italy)*

Secondary low energy (0-20 eV) electron emission under photons and charged particles bombardment is a phenomenon known from well over a century but the mechanisms responsible for it are not yet fully clarified. In solids, one of the most efficient channels of electron impact energy transfer is the excitation of volume or surface plasmons. Plasmons decay via interband transitions and the consequent emission of an electron in the secondary energy region was proposed in the late 70's¹, recently more complex decay mechanisms have been elaborated². To establish the relative relevance of these secondary electron generation channels is of importance to many branches of fundamental and applied science but direct experimental evidences supporting either model are lacking. Electron-electron coincidence experiments, (e,2e), are one of the most complete ways to investigate plasmon creation and decay mechanisms³. The Roma Tre group has been aiming to this target by performing (e,2e) and (g,2e) plasmon assisted low energy electron emission experiments on Al^{4,5} and Be⁶ clean surfaces and CuPc/Al(100) interface⁷. The coincidence measurements reveal the emission onset at an energy corresponding to the Al Fermi level and a pronounced peaks corresponding to the emission from the Al and Be surface states. These results indicate that bulk (or surface) plasmon decays transferring completely its energy and momentum to a single electron in analogy to the photoemission process. This plasmon resonant channel competes with direct electron-electron impact generation of secondary electrons⁸. The Be experiment⁶ performed at constant binding energy of the single particle initial state, clearly shows that the plasmon resonant channel dominates over the direct impact one in generating secondary electrons. Here we present the principal results on the emission of low energy electrons in the secondary energy region related to the decay of a surface or bulk plasmon obtained by the Roma Tre group.

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#015 - Transparent conducting and phase change oxides: new classes of plasmonic and hyperbolic metamaterials*Arrigo Calzolari - CNR-NANO-S3 Istituto Nanoscienze, Centro S3 Modena**Other Authors: Alessandra Catellani (CNR-NANO-S3 Istituto Nanoscienze, Centro S3)*

The research of new plasmonic materials [1], alternative to standard noble metals, for the realization of photonic devices in the THz-to-visible range is continuously increasing. In this regard, new classes of materials such as transparent conductors and phase change materials (PCMs) have been proposed as promising plasmonic and/or hyperbolic metamaterials in the visible and infrared (IR) range. From one hand, transparent conductors (TCs) are electrical conductive materials with a low absorption of light in the visible range. The unique combination of metallicity and transparency makes them appealing for a variety of optoelectronic applications. TCs are obtained by doping wide band-gap semiconductors with metal ions. Yet, the remarkable combination of conductivity in an albeit wide-gap (transparent) material is not fully understood, along with the effect of dopants and defects on charge transport and reflectivity. On the other hand, PCMs can undergo electronic and structural transitions, upon thermal, electrical, chemical or mechanical excitations. Materials that undergo metal-insulator transitions are particularly appealing as they radically modify their electrical and optical properties. This unique property is largely used to realized multi-switchable photonic devices such as plasmonic nanoantennas, ultrafast light emission modulators and near-field thermal transfer devices.

By using first principles approaches based on DFT for the characterization of single materials and effective medium theory (EMT) for the characterization of composites, we present the plasmonic properties of two different classes of metal-oxide materials: transparent conducting oxides (Al-ZnO and Ta-TiO₂) and metal-oxides PCM (VO₂). In the first case, we investigate the microscopic effects of metal doping (e.g. Al, Ta) [2] and defects (e.g. vacancies) [3-4] on the optical and electronic properties of TCOs and how this reflects on the plasmonic response of surface-plasmon polaritons or layered hyperbolic metamaterials, in connection with other dielectric media (e.g. ZnS, etc). In the second case, we focus on planar homostructures resulting from the coexistence of metallic and semiconducting phases of VO₂. This joint-phase combination, which has been experimentally realized, gives rise to an optical metamaterial without the introduction of other different media. This homojunction exhibits tunable optoelectronic properties, with highly anisotropic permittivity, and type-II hyperbolic behaviour in the mid-IR [5]. The possibility of generate volume-plasmon polariton waves in VO₂metamaterial is eventually discussed.

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#016 - OAM resolved EELS spectroscopy of plasmonic nanoparticles

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Low loss EEL spectroscopy in TEM is one of the main techniques to study localized surface plasmon resonances (LSPs) in metallic nanostructures, enabling a mapping of the electromagnetic fields associated to these excitations with nanometric resolution [1]. In such experiments the measured physical quantity is the loss probability density function, as a function of the probe position on the sample: it enables to evaluate the absolute value of the projection of the electric field associated to the excited plasmon along the optical axis.

This approach doesn't lead to a complete understanding of the symmetry properties of the plasmonic resonances, especially in the case of excitations with close energies and similar electric field distributions. This problem can be overcome by shaping the electronic wavefunction to match the symmetry of a given LSP, in order to detect only that peculiar mode while excluding other excitations without the required field distribution [2].

In this work we study the LSPs symmetries by measuring both the energy and the orbital angular momentum of the electrons which have inelastically interacted with the metallic nanostructure: we have started from the theory exposed in [2] and we have computed OAM resolved loss functions within the non retarded approximation [1], evaluating the spatial and spectral properties of the plasmonic modes through MNPBEM toolbox [3].

As a first example we focus on the case of systems with cylindrical symmetry as nanodisks and we point out that a post selection in terms of the OAM immediately enables to classify LSPs according to their multipolar order.

The post selection in OAM also permits to obtain more insight in the way in which the plasmon modes are modified, once the cylindrical symmetry is broken: as suggested in [4] the new plasmonic modes can be obtained by mixing LSP of the original cylindrically symmetric system to find new hybridized modes. We demonstrate that such mixing is effectively measurable by probing the OAM of the inelastically scattered electrons and so good control in the change of the plasmonic properties of a given nanostructure under morphing is available.

Finally, as already exposed in [5], strong differences in the intensity of the loss functions corresponding to opposite OAM are expected in chiral assemblies of metallic nanoparticles. Selecting the inelastically scattered electrons in terms of their OAM provides insights in the properties of chiral plasmonic nanostructures.

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#017 - CdSe Quantum Dots endowed with a long-lived luminescence as result of reversible electronic energy transfer

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The reversible electronic energy transfer (REET) has been investigated in a wide range of molecule-based bichromophore systems, including molecular dyads [1] and non-covalent assemblies [2,3]. Such a process occurs at room temperature only if the electronic excited states of both the donor and the acceptor are energetically close enough (i.e., $\Delta E \approx 0.1$ e.V.) Colloidal luminescent semiconductor nanocrystal quantum dots (QDs) have the enormous advantage that their emitting state can be tuned by manipulating their size, thus providing a significant accuracy in designing and developing of REET-based systems. Herein we report the first example of REET occurring between QDs and a suitable organic chromophore attached to their surface. In our nanohybrid system the emitting state of a suitably synthesized CdSe QD sample undergoes an equilibration with the energy-matched lowest triplet excited state of 1-pyrene carboxylic acid (1-PCA), which ultimately gives rise to an unprecedented thermally activated delayed photoluminescence from the nanocrystals and, as a consequence, to the elongation of their lifetime by several orders of magnitude. Strong experimental evidences of the effect of the oxygen and of the size of the QD were also observed [4].

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#018 - Symmetry enhances non-reciprocal polarization rotation in a terahertz metal-graphene metasurface

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In the present contribution we numerically investigated the magneto-optical behaviour of a subwavelength structure composed by monolayer graphene and a metallic metasurface of optical resonators. By means of this hybrid graphene-metal structure, a large increase of the nonreciprocal polarization rotation of graphene can be achieved over a broad range of frequencies in the terahertz range. Intriguingly, we demonstrate that the symmetry of the resonator geometry plays a key role for the performance of the system: in particular, increasing the symmetry of the resonator the nonreciprocal properties can be progressively enhanced.

To unequivocally quantify the performance of the polarization rotation, we relied on a formalism which links the rotatory power - insertion loss compromise with intrinsic properties of the magneto-optical material – here the graphene. In detail, we evaluated the Faraday rotation figure of merit and compared it with the upper limit employing the formalism given in [1]. Notably, the figure of merit gets closer to the limit as long as the symmetry degree of the resonator attains higher levels. Operation in both transmission and reflection with almost the same performance in different frequency ranges is possible.

The proposed system is hence a subwavelength, tunable, multifunctional, effective nonreciprocal element in the terahertz region. It will enable, among others, lightweight, compact and efficient optical isolation in quantum-cascade laser systems.

- [1] M. Tamagnone et al., *Fundamental limits and near-optimal design of graphene modulators and non-reciprocal devices*, *Nat. Photon.* **8**, 556 (2014)

#019 - Tunable out-of-plane excitons in 2D single crystal perovskites

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Hybrid organic-inorganic perovskites have emerged as very promising materials for photonic applications, thanks to the great synthetic versatility that allows to tune their optical properties. In the two dimensional (2D) crystalline form, these materials behave as multiple quantum-well heterostructures with stable excitonic resonances up to room temperature.

Here, we observe strong exciton-photon coupling in 2D hybrid perovskite single crystal waveguides and we use polarization-dependent exciton-polariton response to assess the nature of the elementary excitations of these systems. For the first time, we observe an out-of-plane component of the excitons, unexpected for such 2D systems and completely absent in other layered materials like transition-metal dichalcogenides or GaAs based quantum wells.

Moreover, we show that the choice of the organic ligands controllably affects the out-of-plane exciton-photon coupling, by changing the inter-quantum well distance and the layer structure. This provides a new route to tune not only the energy but also the orientation and polarization of the transition dipoles in these semiconductors. Such vertical dipole coupling is particularly sought in those systems like plasmonic nanocavities in which the direction of the field is usually orthogonal to the material sheet.

Finally, we show that the layered electronic structure induces an extremely large birefringence that depends on the thickness and the nature of the organic interlayers and we exploit this feature to completely rotate the linear polarization degree in few microns of propagation within the single crystal.

These results show how 2D perovskites provide an ideal platform for developing novel multifunctional materials in which the crystalline architectures can be synthetically tailored in order to provide a huge range of semiconductors with unique properties.

#020 - Plasmon hybridization engineering in self-organized nanostrip dimers

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The engineering of self-organized plasmonic metasurfaces is demonstrated by a maskless technique employing defocused ion-beam sputtering and kinetically controlled metal deposition. Our approach enables the synthesis of periodic sub-wavelength gold nanostrips over large cm^2 area, in a reliable and controllable way. A multi-level variant of the self-organized approach led to high resolution manufacturing of vertically stacked nanostrip dimer arrays, designed by plasmon hybridization methods. In particular, we show the optical response of the nanostrip dimers in the so-called gap-plasmon configuration, demonstrating electric and resonance excitation in the visible (VIS) and near-infrared (NIR) spectrum [1]. The magnetic dipolar mode offers superior sensitivity and field-enhancement as compared to the more conventional electric dipolar one, and the translational invariance of the nanostrip configuration results into a high filling factor for the hot spots. The strong plasmonic response, tunable into the VIS and NIR spectrum, makes such gap-plasmon metasurfaces very attractive for surface-enhanced linear and nonlinear optical spectroscopies. Recently we began exploring the possibility to exploit the nanopatterned soda-lime glass template to confine multi-metal plasmonic heterostructures with different geometries: (i) vertically or laterally stacked Ag/Au dimers in gap plasmon configuration and (ii) laterally stacked and connected Ag/Au "hut-like" structures. Those systems show promising and peculiar EM wave-front manipulation properties which makes them interesting for color routing applications.

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#021 - Gas phase synthesis of plasmonic, core@shell Ag@CaF₂ nanoparticle films: structure, morphology and optical characterization

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Synthesis, study and applications of NanoParticles (NPs) have been playing a major role in material science and technology over the last 20 years, although some important examples of NP presence in manufactured goods can be dated back to ancient history [1]. Realization of NPs with chemical methods is nowadays mainstream, because of the cost effectiveness and scalability. Nevertheless, physical synthesis with a bottom-up approach presents some advantages, especially when a "fine tuning" of the NP properties is required. Physical synthesis can be single-step and ligand-free, and these characteristics can result in a more accurate analysis of the NP structure and of their electronic and magnetic behavior. During the last years we developed a laboratory for the NP synthesis with a magnetron based gas aggregation source and a quadrupole mass filter. The versatility of the NP source allowed us to prepare and study different types of NPs. Moreover, co-deposition and sequential layer deposition methods have been used to obtain core@shell NPs. These methods gave us the possibility of realizing non-native oxide shells [2], and to investigate metal@metal oxide core@shell NPs by varying independently the core diameter and the shell thickness. We report here the results of experimental activity on physically synthesized Ag@CaF₂ and Ag@MgO NP, of technological interest because of the possibility of exploiting the Ag Surface Plasmon Resonance (SPR) in order to increase power cell efficiency in photovoltaic devices [3]. Scanning electron microscopy, in situ X-ray photoelectron spectroscopy and surface differential reflectivity have been used to characterize the NP assembly, relating the SPR behavior with film morphology and core/shell interface properties, emphasizing the importance of an accurate synthesis procedure on the tailoring of the optical properties of these systems.

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#022 - Novel strategies to inhibit corrosion processes for a long-lasting, safe and sustainable conservation of cultural heritage

Gabriella Di Carlo (I) - ISMN-CNR

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The development of innovative materials and methods for the conservation of valuable artefacts and monuments affected by corrosion processes still represents a key issue and an important challenge for the scientific community. At present, further efforts are necessary to satisfy the demanding requirements related to the protective performance, the environmental sustainability and the cost-effectiveness. Specifically, in the field of art conservation, the research of protective materials that can inhibit the degradation processes and preserve the aesthetic properties of the objects and monuments is mandatory.

In this context, within the EU H2020 NANORESTART project “NANOmaterials for the RESToration of works of ART”, we have focused our attention on the development of smart nanostructured coatings able to provide an “active” protection of modern metal works of art and easy to be applied and removed by using not toxic water-based solvents. To achieve a long-lasting and safe protection, we have developed novel coatings based on environmentally friendly polymers from renewable sources, such as chitosan, and with stimuli responsive nano-containers for a tailored release of the corrosion inhibitors. These new materials are more effective and safe than commercial benchmarks, satisfying the aesthetic requirements. Therefore, after validation on model substrates, the developed materials have been applied on real works of art in collaboration with Peggy Guggenheim conservators and their use on other case studies is in progress.

Based on these findings, an approach based on smart nanocarriers is applied to the conservation of concrete monuments within the EU H2020 InnovaConcrete project “Innovative materials and techniques for the conservation of 20th century Concrete-based cultural heritage”. Corrosion inhibitors, properly selected to protect the steel bars, will be confined into the nanocarriers and released under stimuli related to the corrosion processes in the reinforced concrete, such as an increased concentration of chloride ions and a pH decrease. To achieve a long-lasting protective efficacy, the nanocarriers will also contribute to the sequestration of aggressive species by acting as “nanotraps” and hindering their diffusion toward the steel bars.

The InnovaConcrete products after the laboratory validation will be applied on XX century concrete monuments identified as representative case studies that will be fully characterized to get information about the compositional-structural features and their state of conservation. Among the case studies in Italy, War Memorials will be considered for their social values, as symbol of collective identity of European citizens, and relevant monuments in Rome as the Flaminio Stadium by Pier Luigi Nervi will be also investigated.

#023 - Synergism between chemistry and conservation science: the MOLAB experience, from the lab to the museum

Laura Cartechini (I) - ISTM-CNR

Heritage science is an interdisciplinary field encompassing a wide range of competences that now strongly benefits from the synergism established mostly in the last decade between science and conservation. In this context, materials science and analytical chemistry have a primary role for knowledge and conservation of heritage materials.

This contribution is aimed at showing the experience of MOLAB (MOBILE LABORATORY) which demonstrates how now it is possible to obtain excellent results in the study of a variety of heritage objects -with particular attention to paintings- without sampling or moving them to a laboratory. De facto, MOLAB is an integrated platform of mobile instrumentation devoted to non-invasive spectroscopic analysis of artworks *in situ*, offered by some prestigious European Institutions as transnational access to scientists, conservators-restorers, and curators through the program of the Eu project IPERION-CH (Integrated Platform for the European Research Infrastructure ON Cultural Heritage - H2020-INFRAIA, <http://www.iperionch.eu>). The profitable use of a multi-technique methodology, matured in more than ten years of transnational access and based on a solid analytical work in the laboratory both on original artist's materials and on dedicated laboratory model paints, makes it possible a thorough examination of the artists' technique and painting materials and of their present condition by a total non invasive diagnostic approach. Advanced analytical imaging techniques, such as scanning XRF and hyperspectral VIS-NIR imaging, along with other complementary non-invasive spectroscopic tools available in the MOLAB platform (such as UV-Vis-NIR reflectance and fluorescence spectroscopy, reflection FTIR and Raman spectroscopy) allow the identification and mapping of organic and inorganic painting components (including additives and synthesis residues) as well as of their possible degradation products. The same approach also demonstrated to be very useful for monitoring studies of cleaning procedures of paintings, able to assist conservators in the definition of appropriate conservation strategies or researchers developing new methods for conservation. Exemplary case studies will be presented and discussed, with particular focus on the results of a wide research project on the painting “Scream” by Edvard Munch, made in collaboration with the Munch Museum of Oslo.

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#024 - Non-destructive diagnostics of works of art on paper and textile

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The discoloration of paper and textiles, due to the development of oxidized groups acting as chromophores in their chief component, cellulose, is responsible for severe visual degradation.

By using a non-destructive approach based on the combination of optical reflectance spectroscopy and time-dependent density functional theory (TDDFT) *ab-initio* calculations, it is possible to describe and quantify the chromophores in cellulose fibres in a non-destructive way.

Since paper and textiles are optically inhomogeneous materials whose optical response is strongly governed by scattering effects, in order to recover the absorption coefficient of cellulose fibres from *in-situ* non-invasive reflectance measurements a specific approach based on Kubelka-Munk (KM) two-flux theory must be applied.

In order to simulate the optical properties of pristine and oxidized cellulose by using TDDFT, an infinitely extended crystal of cellulose in the crystallographic phase called I_β was considered. Oxidation was simulated by including several kinds of carbonyl groups (ketones, aldehydes, and carboxylic acids) within the β-D-glucopyranose units of pristine cellulose and calculating their electronic transitions.

The concentration of carbonyl groups acting as chromophores was then obtained by fitting the experimental optical absorption spectra to those simulated computationally by using TDDFT-based calculations. In this way quantitative chemical information, such as chromophores concentration, can be obtained, as well as quantitative spectra of additional substances such as pigments or dyes.

This method was applied to several works of art on paper or textiles, in particular, for monitoring the state of conservation of the Leonardo da Vinci's drawings. It was also applied for monitoring conservation interventions of artefacts affected by chromatic deterioration (such as some Renato Guttuso's drawings) submitted to cleaning and reducing treatments at the IC-RCPAL. Results provide fundamental information in order to improve the conservation treatments of works of art on paper.

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#025 - Photophysics of Artist's Pigments

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During the past decades, interest in non-invasive investigations for the characterisation and identification of painting materials has greatly increased. In general, the nature of museum objects is such that sampling is always kept to a minimum and is often completely unacceptable. Therefore, such analyses are more routinely used in the cultural heritage field. Photoinduced luminescence spectroscopy (PL) can provide quantitative information on a small area (e.g. emission properties, PLQY and lifetime). By contrast, photoinduced luminescence imaging provides information on the distribution of materials of interest over large areas. When supported by theoretical (DFT) calculations for the interpretation of the photophysics involved in the luminescence processes, luminescence investigations can

provide useful information for heritage specialists. Photoluminescence investigations of painting materials has proven useful to fields well beyond cultural heritage. For instance, it has been recently demonstrated that Egyptian Blue (a blue ancient pigment) exhibits a remarkable emission intensity in the near-infrared region and has a future in a variety of hi-tech applications including bio-medicine, lasers and telecommunications. Here we report the optical properties of few dyes used in paintworks.

#026 - IRON AGE BLACK GLASS FROM ITALY AND SLOVAKIA: TECHNOLOGICAL EVOLUTION OF EARLY NATRON GLASS VS WOOD ASH TECHNOLOGY.

Sonia Conte - National Research Council - Institute of Science and Technology of Ceramics

Recent studies on Iron Age (10th–8th cent BC) black glasses found in France (Gratuze & Picon, 2006) and Jordan (Reade et al., 2009) demonstrated that they were among the first natron glass varieties ever produced. All these samples share the same chemical features: low K₂O and MgO, very high FeO and low CaO. Consistently, (E)SEM-EDS analyses evidenced the presence of many unmelted grains of heavy minerals (*e.g.* chromite, iron oxides). The present study aims to investigate the chemical-physical features of 96 Iron Age black glass beads dated to the 9th–5th cent BC coming from Torre Galli, Francavilla Marittima, Cumae, Pozzuoli, Sarno and Bologna (Italy), and Chotin (Slovakia). SEM-EDS, EMPA, and LA-ICPMS analyses —as well as that of Sr and Nd isotopes performed on a selection of samples— provided evidences for different production technologies. The black samples recovered in Italy are all natron-based glass probably produced in Egypt, but they can be divided into two groups characterized by the use of different silica sources and recipes. In fact, the oldest samples (9th–8th cent. BC) were produced from very impure iron-rich sands directly mixed with natron, while the more recent ones (7th–6th cent. BC) were made from mature sands – generally used for high-quality natron-based glass – and then colored by the addition of iron oxides. The oldest samples fit therefore the picture for the earliest natron black glass produced with impure sands also found in France and Jordan. Conversely, the more recent samples (7th–6th cent. BC) indicate a technological refinement in the production of the natron glass during the 1st millennium BC. In these latter samples, the choice of mineralogically mature sands with CaO contents high enough to stabilize the glass allowed the production of high-quality glass colored in different nuances, which will bethe technology employed during the subsequent Roman period. The Chotin samples dated to the 5th cent BC, appear very different from the Italian ones, being characterised by low Na₂O, but high K₂O, CaO and P₂O₅, which suggest that wood ash was used as a flux. The colouring technique employed, instead, was the same used for the oldest natron black glass, that is the intentional choice of dark sands. The Chotin wood ash glass has no equivalent among its coeval glass chemical typologies, exhibiting a great affinity with the ‘Early Wood Ash Glass’ produced in central Europe during the Medieval period.

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#027 - Development of SERS substrates for Cultural Heritage applications

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Anthraquinoid dyes, aromatic compounds derived from anthraquinone, have been the most applied red organic colorants in the history of art. Their identification and characterization in artworks, such as textiles, can provide important information for dating, authentication, and conservation treatment of these objects.

Generally, reversed-phase liquid chromatography is the method of choice for the analysis of dyes after a wet sample treatment, since most of their chromophores are polar and water-soluble compounds. Optical spectroscopic techniques cannot be compared with liquid chromatography, in that they do not separate the various components of a dyestuff, nevertheless their ability to rapidly analyze much smaller samples is remarkable in a museum context.

In this study, different approaches based on surface enhanced Raman scattering (SERS) have been evaluated for the analysis of natural organic dyes used in textile dyeing. SERS-active silver nanostructures were produced by electroless galvanic displacement on silicon substrates and by Pulsed Laser Ablation in Liquid (PLAL). PLAL presents some advantages when compared to conventional chemical preparation methods, namely the absence of reagents in the suspension and a higher control over the nanoparticles morphology that can be obtained by changing the ablation conditions. In this work, PLAL nanoparticles were used to prepare disposable paper SERS substrates via drop-casting.

For the application to dyes analysis, two strategies were investigated. In the first, laboratory-dyed vegetable and animal textiles were micro-extracted with a mild aqueous treatment, and the liquid fraction deposited and pre-concentrated on the functionalized substrates. In the second method, concentrated silver nanoparticles were deposited on fiber micro-samples for their direct analysis avoiding any chemical treatment.

#028 - Metals as Canvas: characterization and conservation of painted metal artefacts

Monica Albini - Istituto per lo Studio dei materiali Nanostrutturati (ISMN-CNR)

Other Authors: Gabriel Maria Ingo (ISMN-CNR)

The use of science for the conservation of cultural heritage is nowadays widespread. Many studies have been conducted on artworks made of single materials (e.g. paintings, stones, metals). However, the characterisation and conservation of composite artefacts is a rising research field among European conservation scientists. The project INTERFACE (paINTed mEtal aRteFActs ConsErvation) is now starting and it is focused on composite artworks made of painted metal. Indeed, the particular use of metals as “canvas” has never been investigated even though many masterpieces were created using this technique. Known are the degradation mechanisms occurring to metal artefacts as well as to paints as single materials. However, rare studies about painted metals and paint-metal interactions have been undertaken so far. There is an extended lack of knowledge about the degradation processes that occur on such artefacts and about the conservation methodology to adopt. This project aims to fill this lack of scientific information, having two main objectives:

1. The characterisation of the degradation mechanisms, with particular attention to the processes occurring at the paint-metal interface;
2. The development of a conservation methodology to preserve both paint film and metal substrate.

In particular, the decay mechanisms and the conservation approaches of copper and iron/low carbon steel as substrates decorated with linseed oil paints will be investigated.

The first phase of the project will focus its attention on the permeation of the paint film, on the metal corrosion processes (e.g. differential aeration, cathodic delamination) and on the interaction between the binder fatty acids and the metal substrate at their interface. For the first time the interface area between the paint film and the metallic support will be characterized at micro and nano-scale.

The second phase will be devoted to the development of a conservation methodology for painted metal artworks. Conservators-restorers will be involved to create the best product to consolidate and protect the paint layer and, at the same time, to passivate the metallic substrate.

#029 - Atomistic Scale Modeling of the gas phase synthesis of Silicon and ZnO nanoparticles.

Luca Sementa - National Research Council - IPCF

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Since nanoparticles (NP) are widely applied in many relevant technological areas ranging from electronics to biology, satisfying their increasing request needs processes for large-scale productions. The synthesis by a bottom-up approach based on condensation from low-temperature plasma is a promising technique for the massive production of NP. Furthermore, a gas phase synthesis is particularly attractive because, avoiding the use of solvents, is generally more eco-friendly than other large-scale processes.

Although NP condensation from plasma begins to be used at the industrial level, improving production rates and control of final product properties (particle size, surface area, structure, chemical composition, morphology) is an open problem. Since extracting experimental information on the processes occurring in the plasma reactor at temperatures of thousands of degrees is rather complicated, modeling can be a useful tool for a predictive design.

In this talk I will discuss the results of our efforts in training classical all-atom force fields, against quantum chemistry results, to obtain a reliable description of Silicon and ZnO plasma systems with the final aim to create efficient mesoscale models for the optimization of the production processes. I will show which relevant information can be extracted from molecular dynamics trajectories and used to feed the mesoscale simulations. The discussion will be focused on the role of temperature and pressure on the nanoparticle growth, the origin of the forces that rule the low-temperature plasma dynamics and how the interaction forces are affected by the presence of plasma contaminants.

This kind of information is crucial for understanding the dynamical processes of nucleation and growth and the relative stability of NP of different dimensions that are present in the plasma reactor in order to optimize the selective synthesis of NP with specific features.

#030 - Hydrogen scattering from a cesiated surface model: Vibrationally excited molecules formation and isotopic effect.

Amedeo Palma - CNR - ISMN

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A cesiated surface model was considered to study the dynamics of hydrogen atom scattering by semiclassical collisional method. Using dipole correction method, the work function of the considered surface, is calculated to be 1.81 eV (± 0.02) eV. The Potential Energy Surface for the interaction of H atoms with the surface was determined *via* first principles electronic structure calculations including both the interaction with Cs surface atoms and underlying Mo atoms. We found that the scattered H atoms have a negative partial charge of nearly 0.4 and that the backscattered flux arises mainly by H atoms impinging directly or very close to Cs atom on the surface, while H atoms impinging in the voids between the Cs atoms propagate through the first Cs layer and remain adsorbed. The probabilities for recombination reaction and for the complete set of elementary surface processes arising from different reactions were evaluated. It appears that the recombination occurs with low probability, while for the other site H atoms are mainly scattered from the surface with a partial negative charge [1]. The vibrational distributions of formed H₂ molecules exhibit a non-Boltzmann behaviour and are peaked on medium-high lying vibrational levels. The interaction of deuterium atoms and the formation of hydrogen isotopologues molecules on the surface *via* the Eley-Rideal mechanism is studied using the same computational setup.

The considered surface appears promising for negative ion sources [1,2], contributing to the formation of ions by means of both usually considered mechanisms: surface production and volume production *via* dissociative attachment.

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#031 - Interfacial Charge Density and Its Connection to Adhesion and Frictional Forces

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Friction and adhesion are common phenomena that impact many fields from nanotechnologies to earthquakes, but their fundamental origin is still largely unknown. The reason resides in the fact that even for macroscopic objects, friction and adhesion are governed by microscopic contacts, where the atomistic interactions of quantum mechanical origin ultimately determine the tribological response. Thus, it is of great practical and theoretical importance to understand the connection between the electronic structure and the mechanical tribological properties of interfaces, for example to design new lubricant additives. The functionality of some solid and boundary lubricants is, in fact, based on their capability of decreasing the adhesive interactions between the surfaces in contact.

Here we derive a connection between the intrinsic tribological properties and the electronic properties of a solid interface. In particular, we show that the adhesion and frictional forces are dictated by the electronic charge redistribution occurring due to the relative

displacements of the two surfaces in contact. We define a figure of merit to quantify such charge redistribution and show that simple functional relations hold for a wide series of interactions including metallic, covalent, and physical bonds. This suggests unconventional ways of measuring friction by recording the evolution of the interfacial electronic charge during sliding. Finally, we explain that the key mechanism to reduce adhesive friction is to inhibit the charge flow at the interface and provide examples of this mechanism in common lubricant additives [1].

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#032 - Graphene-based nanostructured models for energy storage

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Graphene-based materials have generated considerable interest in the development of new nanostructured materials to be used as efficient solid-state hydrogen storage devices. Several studies have highlighted the possibility to increase the hydrogen uptake by modulating the porosity and the surface area of these graphene-based materials[1,2]. Therefore, a set of theoretical and realistic models for the graphene based material is required to investigate in more details their properties and eventually to drive experimentalists in making them.

Here we propose and implement an algorithm to generate graphene 3D-scaffold with given porosity and specific density, and realistic structure. The algorithm is based on a stepwise generation of graphene flakes of size, shape and orientation randomly distributed, until the wanted structural features are reached. The structure is subsequently refined by means of molecular dynamics simulations using empirical force fields. Optionally, it can be decorated with adatoms (H, O or others) to mimic the real structures. Finally, the structure is characterized versus its gas adsorption capability by means of grand canonical monte carlo and versus its capability to adsorb ionic liquids by using molecular dynamics simulations.

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#033 - Structure and dynamics of an ionic liquid confined in nanopores

Stefano Mossa - CEA Grenoble- INAC/SyMMES

Ionic liquids are mixtures of cations and anions which stay liquid at room conditions, a feature making them potentially ideal materials for energy storage and conversion technologies. Here they are often employed in contact with solid interfaces, or even constrained in pores whose size can be less than a nanometer. In such extreme environments the properties of matter are drastically modified compared to the bulk counterparts. In this context one can address a primary issue: Does the phase nature of an ionic liquid change when it is confined in pores of nanometric size? The simplicity of this question is misleading. Experiments which probe ionic liquids at the nanoscale, in fact, are extremely difficult and sometimes in mutual contradiction, failing so far to provide a generally accepted answer.

I have tackled this issue systematically by extensive Molecular Dynamics simulation of a model ionic liquid confined in a slit pore[1]. In this talk I will discuss how, by appropriately tuning size and temperature of the latter, I revealed unexplored phase modifications. For instance, following an increase of the confinement, I observed the formation of ionic liquid-crystal structures, which unexpectedly transform into plain stable liquid states and subsequently freeze in new crystal phases. I will also show how these changes reflect on the relative organization of the ions and on their dynamical state. I will finally build on the MD results to provide a consistent general picture of these systems, by also involving in the discussion disparate very recent inspiring work.

[1] Stefano Mossa, Re-entrant phase transitions and dynamics of a nanoconfined ionic liquid, Phys. Rev. X accepted, pre-print arXiv:1803.08888

#034 - Correlation between microstructure and plastic behaviour in low alloyed ductile iron through a deterministic model

Giuliano Angella - CNR-ICMATE

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Ductile irons are attractive materials because of their low cost and wide range of applications. The low cost comes from easy route of production in near-net-shape components through foundry, and from the low content of alloying elements, which is also topical for the critical raw materials issue. Ductile irons are Fe-C-Si alloys with hypereutectic compositions with an appropriate Mg content to produce graphite in nodular shape, in a matrix of bcc ferrite and eutectoid pearlite in different volume fractions. The control of microstructure produced during solidification is a key issue to obtain the optimal plastic behaviour of ductile irons. So nodule counts, nodularity of graphite nodules, ferritic grain size and pearlite volume fractions have to be measured for foundry feedback. Therefore, a deterministic model for the correlation between the measured microstructure and the plastic behaviour is fundamental to understand the microstructure features that actually affect the mechanical behaviour and to produce a helpful feedback to the industrial producer.

Samples of ductile iron GJS 400 have been produced through four different moulds with increasing thicknesses to test the effect of the solidification rate on the final microstructures that have been investigated and quantified through scanning electron microscopy. The samples were also tensile-tested to produce the plastic flow curves that are fundamental for the foundry feedback and also for the component designers. The model used to describe the tensile plastic flow curves are dislocation-density-related constitutive equations and incorporates physical parameters correlated to the microstructural features. The model has been tuned on the ferritic materials produced in the fastest cooling rate and can well predict the tensile plastic flow curves of the samples from the different moulds.

The work that is going to be presented, concerns the research collaboration on the metallurgy of ductile irons between CNR-ICMATE and the foundry Zanardi Fonderie SpA.

#035 - Charge density waves in 2D metal chalcogenides probed by ultrafast and spatially resolved ARPES*Enrico Da Como (1) - University of Bath**Other Authors: Charles1 Sayers1, Stephen1 R. Clark1, Daniel1 Wolverson1 (1Univ. Bath) Jasper2 van Wezel2 (Univ. Amsterdam) Sven3 Friedemann3, Jude3 Laverock3, Neil3 Fox3, Mattia3 Cattelan3 (Univ. Bristol) Hamoon4 Hedayat4, Davide4 Bugini4, Claudia4 Dallera4, Giulio4 Cerullo4, Ettore4 Carpena4 (Politecnico, Milano).*

Most semimetallic transition metal dichalcogenides (TMDs) exhibit phase transitions to a charge density wave (CDW) phase driven by different phenomena: exciton condensation, Jahn-Teller distortion, and Fermi surface nesting. The nature of the CDW transition is relevant in understanding the superconducting state of these materials, often arising in proximity to the CDW phase. In this talk I will address two material systems: Titanium Selenide single crystals (TiSe₂) and heterostructures of TiSe₂ with graphene and VSe₂.

The layered TMD 1T-TiSe₂ has been suggested to host a unique CDW phase transition driven by cooperative excitonic and electron-phonon interactions. Ultrafast spectroscopy uses optical pulses below hundred fs to generate non-equilibrium states where electronic and lattice degrees of freedom respond on different time scales. This possibility is used here to observe a phonon bottleneck in the recovery of the CDW in 1T-TiSe₂ after transient perturbation of the CDW excitons by interband optical excitation. A suitable combination of energy and time resolution provided by a unique time- and angle-resolved photoemission spectroscopy (tr-ARPES) setup allows us estimate the excitonic and lattice contributions to the CDW gap. The emerging picture is that the CDW gap in TiSe₂ is mainly due to the excitonic interactions, but electron-phonon coupling ultimately controls the recovery of excitons.

TMDs can be mechanically exfoliated to monolayer thickness flakes that can be assembled into stacked structures by dry transfer and stamping. We demonstrate the possibility to produce TiSe₂/VSe₂ stacks and study the electronic interactions at their interface by spatially resolved ARPES. The in plane spatial (<100 nm) and energy resolution (<20 meV) offer access to previously unexplored electronic states directly in momentum space.

#036 - Spectroscopic and laser emission properties of Yb doped mixed (Lu,Y)2O3 sesquioxide ceramics*Guido Toci - INO-CNR**Other Authors: Angela Pirri (IFAC-CNR, Italy) , Barbara Patrizi (INO-CNR, Italy), Roman N. Maksimov (IEP UrB RAS and Ural Federal University, Russia) , Vladimir V. Osipov (IEP UrB RAS, Russia), Vladislav A. Shitov (IEP UrB RAS, Russia), Artem S. Yurovskikh (Ural Federal University, Russia), and Matteo Vannini (INO-CNR, Italy)*

Yb³⁺ is a well assessed laser dopant for hosts as crystals, fibers and ceramics. Due to its favorable features, Yb lasers are widely used for industrial applications. The available Yb doped materials can produce ultrashort laser pulses with duration down to about 100 fs. The development of new Yb doped laser media with broader emission band will allow the generation of even shorter pulse durations.

Recent studies have addressed several mixed hosts because a disordered lattice structure may induce an inhomogeneous spectral broadening on emission spectra with respect to pure structures. Among the Yb-doped materials, the laser emission of several mixed compositions, both ceramics and crystals has been tested. Yb doped mixed sesquioxide crystals show a significant broadening in the emission spectrum, very useful for the development of ultrafast laser sources.

Transparent ceramics are acquiring increasing importance as laser hosts, for several reasons: their fabrication usually require lower processing temperatures than conventional crystal growth techniques; this is convenient for the fabrication of materials with high melting point such as sesquioxides and some garnets.

We demonstrated highly efficient laser emission of Yb:(Lu,Y)₂O₃ ceramic samples with formula (Yb_xLu_yY_(1-x-y-z)Zr_z)₂O₃ (*i.e.* Yb doped solid solution of Y₂O₃ and Lu₂O₃ with Zirconia as sintering aid) fabricated by means of sintering of mixed sesquioxide nanoparticles under vacuum. The samples were prepared at the Institute of Electrophysics (Russia), and tested at INO-CNR and IFAC-CNR (Italy). The spectroscopic characteristics were investigated, resulting in intermediate properties between Yb:Y₂O₃ and Yb:Lu₂O₃. Laser emission properties were investigated under quasi-CW and CW longitudinal pumping, using a fiber coupled semiconductor laser as pumping source. The highest slope efficiency obtained is 35.1% while the lowest laser threshold is 0.8 W (T=4.7%). The laser emission can be tuned over a very broad range (from 992 nm to 1089 nm, *i.e.* 97 nm).

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#037 - Anisotropic properties induced by self-doping in novel 3D stoichiometric molybdenum oxides*Eugenio Lunedei - Institute for the Study of Nanostructured Materials**Other Authors: Meriem Goudjil, Djillali Mezaoui (Institute of Chemistry/Univ. of Sciences and Technology USTHB, Algiers, Algeria) Paola Bonazzi, Luca Bindi (Dipartimento di Scienze della Terra, Università degli Studi di Firenze, Firenze, Italy) Paola Franchi (Department of Chemistry, University of Bologna, Bologna, Italy), Andrea Migliori (CNR-IMM, Bologna, Italy), Giampiero Ruani Francesco Mercuri (CNR-ISMN, Bologna, Italy)*

Transition metals oxides, in particular molybdenum oxides, are extensively studied among the key compounds of many organic/inorganic interfaces in device physics. This class of oxides is generally characterized by anisotropy in vibrational, optical and charge transport properties. Many of these compounds are non-stoichiometric, therefore difficult to be theoretically studied via *ab initio* methods. Their properties cannot be generally derived, in an easy way, from the atomic structure.

With the aim to create a model system for studying the physical origin of the anisotropic properties, we developed a number of novel 3D stoichiometric oxides. Their structure is based on MoO₆ octahedral framework containing extra cations (As³⁺) as doping centers. The defined stoichiometry allows numerical simulations, whilst the presence of electron doping centers enables a fine tuning of the transport properties of the compounds.

By means of solid state process we grew a number of single crystals characterized by the presence of pseudo-hexagonal cavities. These tunnels, containing chains of As³⁺ and additional O atoms, are separated by 2 or 3 octahedral MoO₃ slabs. Arsenic cation acts as electron donor, whilst a Mo⁵⁺ (for a Mo⁶⁺) accounts for the formula neutrality. These compounds belong to the class of Intergrowth Tungsten Bronzes (ITB).

Low temperature EPR spectroscopy showed a strong paramagnetic signal, proving the existence of (Mo⁺⁵) active centers. High Resolution TEM (HRTEM) images and electron diffraction patterns were in perfect agreement with the crystal structure as determined by single crystal X-ray diffraction analysis. The crystals showed no intergrowths or impurities.

We carried out temperature dependent (300K-12K) electrical conductivity, polarized micro-Raman, optical and impedance spectroscopy along different directions on single crystals. We measured strongly anisotropic Raman signals, a semiconducting behavior with distinct transport regimes and activation energies of the order of few tens of meV.

The transport properties exhibited a quasi-1D character along particular crystalline directions. The band structure, the total and projected density of states and the vibrational frequencies of the system were calculated by Density Functional Theory (DFT), allowing to correlate the electronic properties to the crystal structure. Polarized Raman modes were identified according to the crystal symmetry.

The crystals showed a charge density distribution characterized by reduced dimensionality, with charge segregation in layers parallel to defined crystal planes. The knowledge acquired from the study of these peculiar 3D model systems can be applied to the comprehension of transport properties in 2D layered oxides.

Keywords: Molybdenum oxide, single crystal, EPR, polarized Raman, DFT, Band structure, temperature dependent transport properties.

#038 - Molecular-level investigation of receptor-ligand interaction at interfaces

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Molecular recognition is a recurrent issue in chemical sensing because of the importance of selectivity for sensor performances. The progress made in mastering weak interactions has enabled the design of a large pool of synthetic receptors, according to the analytes to be detected, which however has not had a significant impact on sensors technology. This gap has emerged because of the difficulties in transferring the intrinsic molecular recognition properties of a given receptor from solution to interfaces, preserving the functional conformation and orienting the binding fragments toward the analyte-containing phase, in order to reduce nonspecific dispersion interactions. The main reason is the lack of characterization techniques capable of directly probing receptor-ligand association at interfaces.

To fill this gap, we report the first in-situ analytical investigation of molecular recognition at the solid-gas and liquid-gas interfaces, carried out through Sum-Frequency Vibrational Spectroscopy (SFVS), a versatile tool for non-invasive probing of any interface accessible by light, with chemical selectivity, intrinsic surface specificity and sub-monolayer sensitivity. In particular, we investigate the complexation capability of surface-bound organic macrocyclic receptors, namely tetraquinoxaline cavitands (QxCav) and ethylene-bridged tetraquinoxaline cavitands (Et-QxBox), exposed to aromatic and aliphatic compounds at the air-water and solid-air interfaces. By probing the molecular fragment involved in the host-guest association, SFVS allows to correlate the molecular architecture of the receptor-decorated surface with the orientation of the complexed cognate analyte inside the binding pocket. The study, which can be readily extended to other receptors, interfacial architectures and analytes, proves that SFVS is able to provide a molecular-level understanding of host-guest complexation at interfaces, close to the actual environment for sensing applications.

#039 - Intramolecular Charge Transfer, Relaxation Processes and Solvation Dynamics in 4,7-bis (4,5-dibutylbenzo[1,2-b:4,3-b']bisthiophene[1,2-b:4,3-b']bisthiophen-2-yl)-2,1,3-benzothiadiazole

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We report a combined approach of stationary and time resolved fluorescence measurements, UV-Vis transient absorption spectroscopy along with *ab-initio* calculations which provide an overall picture of the dynamics occurring after excitation in a push-pull molecule, namely 4,7-bis (4,5-dibutylbenzo[1,2-*b*:4,3-*b'*]bisthiophene[1,2-*b*:4,3-*b'*]bisthiophen-2-yl)-2,1,3-benzothiadiazole. The analysis of the emission spectra in solvents of different polarity reveals the presence of three conformers whose structures differ for the orientation of the 4,5-dibutylbenzo-bisthiophenegrups and for their planarity respect to the benzothiadiazole acceptor group. Kowski method allows us estimating ground and first excited states dipole moments (μ_g and μ_e) for the three conformers. We find values of μ_e similar for the three conformers and higher than the relative μ_g values as can be expected from a push-pull molecule undergoing a light induced charge transfer (CT) transition. UV-Vis transient absorption spectroscopy in different solvents highlights the instantaneous (within our instrumental resolution) formation of a Locally Excited- S_1 state (accompanied by a big change in the dipole moment respect to S_0) which undergoes a rapid Intramolecular Charge Transfer assisted by molecule planarization (PICT). The strong dipole-dipole interactions with the polarized solvent molecules stabilize the S_1 CT state that decays principally through fluorescence emission. Both PICT and solvation dynamics are responsible for the big Stokes' shift characterizing the molecule, particularly in polar solvents. The fluorescence lifetimes are substantially longer in polar solvents than in non polar ones as well as fluorescence quantum yields are higher. We conclude that the radiative relaxation time increases when a molecular planarization of the S_1 emissive state takes place and this condition is more favoured in polar solvents where local dipole-dipole interactions support the structural stabilization of the CT emissive state. In PMMA matrix the structural and solvation dynamics are strongly inhibited leading to a reduction of non-radiative processes and to a shortening of the fluorescence relaxation time.

#040 - Brillouin Optical Time Domain Analysis with Pump-Probe Scheme Employing a Low-Noise Brillouin Ring Laser

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Strain and temperature distributed sensing systems based on Brillouin optical time domain analysis (BOTDA) have become of widespread adoption, since they allow for accurate measurements along more than 100 km long optical fiber spans. In typical BOTDA schemes, a pulsed lightwave signal (pump) and a downshifted CW signal (probe) are injected in opposite directions in the sensing fiber, with a frequency shift that lies within the Brillouin gain spectrum (BGS) of the fiber. Phonon-mediated stimulated Brillouin scattering (SBS) transfers a fraction of the pump power to the probe with maximum efficiency for frequency shift equal to the BFS of the sensing fiber, approximately 11 GHz for standard SMF. At one end, the probe trace is recorded for different frequency shift values, and is used to reconstruct the BGS distribution with a spatial resolution defined by the pump pulse temporal length. In BOTDA schemes, the techniques that are commonly employed for tuning the pump-probe shift are based on Phase-Locked Loop (PLL) or optical side-band (OSB) generation method that necessitate costly devices in addition to those employed in interrogator and sensor blocks. In particular, two tunable coherent lasers and a wide bandwidth (more than 10 GHz) electro-optic modulator (EOM) are required for PLL and OSB techniques, respectively.

In this work we report the results of a theoretical and experimental study that we have carried out on a BOTDA sensor that employs an innovative solution for the generation and tuning of the pump-probe signals used to interrogate the sensing fiber. In this scheme, a Brillouin ring laser (BRL) is used to generate the probe signal having a frequency that is downshifted, with respect to the optical pump, by the ring fiber BFS. Since the probe frequency lies automatically in the BGS of the sensing fiber, the tuning range required to sweep the entire gain spectrum is less than 200 MHz. The short cavity doubly resonant (SC-DR) BRL layout, allowed for the mitigation of the mode-hopping effect and obtain low phase and low relative intensity noise (RIN) values. In particular, probe signal has a spectral linewidth of approximately 20 kHz and RIN values of -130 dB/Hz over 800 MHz frequency range. An active wavelength-locking scheme has been used to further stabilize the pump-probe frequency shift and fine tune, with sub-kHz precision, its values across the BGS to reconstruct the gain profile distribution. *

An experimental analysis of the performance of the BOTDA scheme employing the low noise BRL solution has been carried out to measure the strain and temperature accuracy and spatial resolution of the novel sensor. Furthermore, we have performed a comparative analysis among the performance of the BRL based interrogation scheme and the long cavity BRL scheme that we have previously demonstrated in order to evaluate the benefits of the enhanced performance short-cavity laser solution.

#041 - Mode-locking in random lasers

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Recent theoretical achievements allow for a predictive description of nonlinear optical systems in random media in terms of statistical mechanical models. Among them, random lasers. Guided by such theory we experimentally investigated the emissions of the cavity-less random laser made of a powder of GaAs crystals, both in space and wavelength. Through a detailed analysis of multi-mode correlations we provide clear evidence for the occurrence of nonlinear mode-coupling in such random laser its self-starting mode-locking nature as the lasing threshold is overcome. GaAs emission spectra are analyzed by multi-Gaussian fitting and all relevant resonant peaks are identified by means of the Akaike information criterion. The behavior of multi-point correlations among intensity peaks is tested against the nonlinear frequency matching condition underlying phase-locking in ordered mode-locked ultrafast lasers.

Theory predicts frequency matching also in the case of optically active random media, whose modes exchange disordered couplings, though this is not leading to ultra-short pulses, as in standard "ordered" mode-locking ultrafast lasers. Nontrivially large correlations, with respect to background ones, are meant to correspond to interacting mode sets. These are clearly observed for spatially overlapping resonances, who also turn out to sensitively depend on the frequency matching parameter, eventually showing the occurrence of non-linear mode-locked mode interaction.

#042 - Supra and sub molecular investigation of fiber-like soft materials by X-ray scanning microscopy*Cinzia Giannini (I) - Istituto di Cristallografia - Consiglio Nazionale delle Ricerche**Other Authors: Cinzia Giannini*, Alberta Terzi, Teresa Sibillano, Davide Altamura, Dritan Siliqi, Massimo Ladisa, Francesco Scattarella, Liberato De Caro Istituto di Cristallografia – Consiglio Nazionale delle Ricerche - Via Amendola 122-O Bari – Italy Email: cinzia.giannini@ic.cnr.it*

An important group of soft materials, such as collagen, fibroin or lysozyme, naturally orient in fibers with the axes of the long polymeric structures parallel to each other and intrinsically defined. Conversely, in the case of engineered materials, the long molecules are induced to form oriented fibers by different orientation methods (mechanical pulling, electric or magnetic fields), when they do not self-assemble. X-ray fiber diffraction is the ideal tool to inspect their hierarchical organization, from atomic to nanoscale. The experimental set-up is rather simple: the oriented fiber is placed in a collimated x-ray beam at right angles to the beam, and the fiber diffraction pattern is recorded on a detector placed centimeters/meters far from the fiber, depending on the peculiar interplanar distances to be measured (1-2 meters are needed to access nanometric distances with typical hard X-ray energies). When X-ray microsources are used [1], the fibers can be also spatially mapped with the microprobe to investigate their lateral inhomogeneity [2]. In this presentation, selected case studies of fiber diffraction with X-ray scanning transmission microscopy will be reported: *i*) phenylalanine-based fibers [3]; *ii*) bovine and equine collagen [4]; *iii*) fibroin; *iv*) cellulose.

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#043 - Characterization of Blue-shifting Hydrogen bonds in small complexes*Pier Luigi Silvestrelli - Università di Padova*

The so-called "improper blue-shifting" Hydrogen bond, characterizing some small complexes, is theoretically investigated by first-principles calculations based on the Density Functional Theory.

Structural, energetic, electronic, and electrostatic properties are computed not only for complexes with linear Hydrogen bonds but also for systems with multiple intermolecular contacts leading to the formation of "bifurcated" or even "trifurcated" Hydrogen bonds.

In particular, Hydrogen bonds are characterized in terms of differential electron densities distributions and profiles, and of the shifts of the centres of Maximally localized Wannier Functions. The information from the latter quantities can be conveyed into simple geometric bonding parameters that are helpful in characterizing the interatomic bonds.

The effect of including dispersion corrections for describing blue-shifting Hydrogen bonds is also investigated.

Detailed comparison of the properties of systems with blue-shifting Hydrogen bonds to those of others, where more conventional red-shifting Hydrogen bonds are formed, supports the view that there is no fundamental difference between the two kinds of bonds.

#044 - Stacked arrangements of DHI-like monomers as a model of out-of-plane complexity in eumelanin protomolecules*Elena Molteni - Università degli Studi di Milano*

Other Authors: Giancarlo Cappellini (Department of Physics, Università degli Studi di Cagliari, and Istituto Officina dei Materiali CNR-IOM, UOS Cagliari, Italy), Giovanni Onida (Department of Physics, Università degli Studi di Milano, Italy, and European Theoretical Spectroscopy Facility ETSF), Guido Mula (Department of Physics, Università degli Studi di Cagliari, and Istituto Officina dei Materiali CNR-IOM, UOS Cagliari, Italy)

Eumelanin displays a characteristic continuous UV and visible absorption spectrum, with intensity increasing with frequency (e.g.[1,2]), in agreement with its function as a photoprotective pigment. It is known to contain 5,6-dihydroxyindole (DHI), 5,6-dihydroxyindole-2-carboxylic acid (DHICA) and their various redox forms and tautomers as basic building blocks. Although the three-dimensional (3D) structure of eumelanin is not known, experimental evidence points to the presence of π -stacked arrangements of oligomers of the above-mentioned molecules in the pigment. The observed spectral features of eumelanin can not be directly explained in terms of absorption spectra of the small DHI-like monomers, and must thus result from their complex 3D arrangement in the pigment (in-plane oligomerization and out-of-plane stacking), and/or from their chemical heterogeneity.

Stacked arrangements of DHI-like monomers can therefore be interesting as simple models of out-of-plane complexity in the eumelanin pigment, considered as complementary to in-plane oligomerization, and of its role in the transition from the optical properties of small molecules such as DHI to the peculiar absorption spectrum of eumelanin.

In this work we address the optical properties of stacked forms of four DHI-like monomers: 5,6-dihydroxyindole (DHI), 5,6-dihydroxyindole-2-carboxylic acid (DHICA), indolequinone (IQ) and quinone-methide (MQ). We adopt a first-principle approach based on plane-wave (PW) density functional theory (DFT) and time-dependent DFT (TDDFT), investigating the sensitivity of optical absorption spectra to the chemical species, the stacking geometry and the interlayer distance.

Apart from its biological role, eumelanin has also drawn attention in view of possible applications, e.g. in photovoltaics: in this context, eumelanin / porous silicon (PSi) interfaces are currently a subject of experimental work[3,4], and the energetics and electronic properties of simplified models of such interfaces, consisting in tetramers of DHI-like molecules adsorbed on the Si(001) surface, have been computationally studied[5]. I will show preliminary results of our calculations on the optical properties of selected Si(001):tetramer systems.

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#045 - Coarse-grain simulations of mechanically induced transformations in supported lipid bilayers and micelles at heterointerfaces.

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Supported lipid bilayers (SLBs) mimicking biological membranes are synthetic surface biosystems with a great potential for fundamental biophysical studies and applied biomedical research. One of the most important parameters among those influencing the behaviour of biological and biomimetic SLBs is their lipid composition, in turn determining their mechanical characteristics. Atomic Force Microscopy (AFM)-based Force Spectroscopy performed in liquid is an ideal tool for the nanoscale mechanical investigation of SLBs. Force-displacement curves clearly show the sequential compression of each of the two lipid layer. Finer details suggest that the lipid layer can undergo to a phase transition under the influence of the tip-induced local pressure. Nevertheless, lack of atomic resolution in AFM measurements hinders the full understanding of this phenomenon. Quasi-atomistic coarse-grain (CG) computational simulations have been proven to be an essential tool for the study of the mechanical properties of complex lipid assemblies[1]. Allowing to span much larger time and size domains when compared to normal atomistic simulations, CG simulations enable the investigation of complex bio-inspired systems. In particular, the well-established CG MARTINI[2] force field has been extensively employed to model the mechanical properties of lipid membranes. In this work, we perform large scale CG simulations of SLBs of different composition deposited on prototypical supporting surfaces. We show that computational simulations are able to discriminate between mechanical response of SLBs composed of lipids with different degree of saturation in the lipophilic tails and to reproduce the behaviour of mixed structures. Lastly, we show how these results are easily ported to more complex systems in which the bilayer is topologically closed such as synthetic nano-micelles. The results achieved for these prototypical structures, pave the way for simulating more realistic biological systems like extracellular vesicles. References: [1] H. I. Ingólfsson, C. Arnarez, X. Periole, S. J. Marrink, *Journal of Cell Science*, (2016), 0, 1-12. [2] D. H. de Jong, G. Singh, W. F. D. Bennett et al., *Journal of Chemical Theory and Computation*, (2013), 9, 687-697.

#046 - Vibrational and optical fingerprints of conjugated biradicals from DFT and TDDFT calculations*Sofia Canola - INSTM UdR Bologna and University of Bologna**Other Authors: Juan Casado (Department of Physical Chemistry, University of Málaga, Andalucía-Tech), Fabrizia Negri (Dipartimento di Chimica "G. Ciamician", University of Bologna and INSTM, UdR Bologna, Bologna)*

Open-shell singlet biradicals, namely molecules bearing two electrons in degenerate or nearly degenerate molecular orbitals, display unique and interesting properties such as magnetic activity, ambipolar charge transport due to their small HOMO-LUMO gap, absorption spectra towards the near infrared region, significant two photon absorption cross sections due to their favorable non linear optical properties, and singlet fission. Such systems are usually unstable and highly reactive intermediates, however, recently several examples of stable open-shell systems with singlet biradical character have been synthesized and characterized. [1] Many of these molecules are quinoid systems, as naphthoquinoids and quinoidal oligothiophenes, or belong to the class of PHs, pi-conjugated polycyclic hydrocarbons, as for example zethrenes, anthenes and rylenes; in particular, longer members of the last class of compounds, thanks to their arm-chair and zig-zag edges, represent molecular models of graphene nanoribbons.[1] While very detailed experimental spectroscopic characterizations have been reported including Raman and optical activities [2-4], computational investigations were essential to demonstrate the presence of a low lying double exciton state [5], a feature that has become a fingerprint of open-shell singlet ground states.[6] In this study we report the results of computational investigations carried out with two aims: on one hand, we employ spin-flip and open-shell TDDFT calculations to identify the double exciton state for very large conjugated biradicals [7]; on the other hand, we discuss computed Raman spectra of increasingly longer rylene derivatives.[8]

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#047 - Electrical conductivity and charge-transport quantization in ionic fluids*Federico Grasselli - Scuola Internazionale Superiore di Studi Avanzati - SISSA**Other Authors: Stefano Baroni (SISSA – Scuola Internazionale Superiore di Studi Avanzati and CNR-IOM, 34136 Trieste, Italy)*

The Green-Kubo theory of linear response[1] allows to extract the electrical (ionic) conductivity of electronically insulating fluids from the time-correlation function of electric currents, in molecular dynamics simulations.

Standard methods to compute ab initio currents are based on the calculation of Born effective charge tensors of each atom at each time, a computationally demanding operation. Interestingly enough, the same results are obtained if Born tensors are replaced by integer oxidation numbers of the atoms[2].

We discuss how arguments from charge-transport quantization[3] and from a recently-formulated gauge-invariance principle of transport coefficients[4] can be employed to understand this strange coincidence, providing an alternative method to compute first-principle electrical conductivity of ionic fluids[5]. Explicit examples and numerical experiments are given for the case of molten potassium chloride.

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#048 - Assessing the role of the proton scavenger for PEDOT molecular weight and morphology: an atomistic investigation.

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Other Authors: A. Antidormi, A. Bosin, D. Galliani, D. Narducci, C. Melis

Thermoelectric devices are promising and environmentally friendly systems to recover energy from industrial waste heat or natural heat. Organic semiconductors represent promising candidates as thermoelectric materials due to their peculiar features: low thermal conductivity, high flexibility and low cost. However, the exact impact of how synthesis can impact on morphology and thus on thermoelectric figure of merit of organic conjugated polymers is still not well understood. Crucial informations can be obtained by means of an atomistic computational approach by obtaining a microscopic scale description of the polymerization process which is presently not experimentally available. In this work, we present a novel computational tool to model the polymerization process, assuming a chain growth mechanism simulated by means of a combination of density function theory and classical molecular dynamics methods, without any educated guess about the evolution, which is energetically driven. Standard formation energies are calculated using DFT methods in different chemical environment and varying reactants stoichiometry. After polymerization has happened, different morphological analysis are carried on for system of about $1E5$ atoms and several tenths nanometers, focusing on how the followed polymerization path affects final properties. We present the results of the application of the above procedure to the case of poly(3,4-ethylenedioxythiophene)-Tosylate (PEDOT-Tos) under several experimental conditions i.e. different solvents, oxidants, and temperatures. The overall effect on the morphological and thermoelectric properties will be discussed.

Materials and Modelling for Energy Conversion	Vittorio Privitera
Materials and Processes for Environment Protection and Sustainability	Alessandra Sanson
Molecular self-assembly and supramolecular materials	Alberto Credi
Organic/Hybrid and Printed Electronics and Photonics Pietralunga	Silvia Maria
Poster Session October 23	
Materials and Processing for Energy	Giampiero Ruani
Biomaterials for Regenerative Medicine	Gino Ambrosio
Molecular self-assembly and self-organized nano and mesostructures	Alberto Credi
2D Materials for Energy and Environmental Applications	Vittorio Privitera
Materials and Processing for Energy	Michele Maggini
Materials and Processes for Environment Protection and Sustainability	Alessandra Sanson
Biomaterials for Regenerative Medicine/Additive Manufacturing in Biomedical Research and Active Packing Materials	Gino Ambrosio

#049 - Water-processable nano-assemblies based on amphiphilic low band gap rod-coil block copolymers for sustainable organic solar cells

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Water-processable organic nanoparticles (NPs) of semiconducting polymers are receiving wide attention for optoelectronic applications due to their simple fabrication and tunable properties. The NP-based approach is appealing to control the morphology of the active layer in optoelectronic and electronic devices, such as organic photovoltaics (OPVs), organic light-emitting diodes, and organic field-effect transistors. [Organic Electronics: Emerging Concepts and Technologies, 2013, Wiley-VCH] The miniemulsion method ensures the stability of the water-suspended NPs using insulating surfactants, lowering the chlorinated solvent use for the active layer fabrication. To gain good performances, the surfactant excess has to be removed at the end of the process. [Mater Today 2016, 19, 533]

Here we will present a series of amphiphilic rod-coil block copolymers (BCPs), constituted by a low band-gap polymer, PCPDTBT as electron donor material, and different poly-4-vinylpyridine (P4VP)-based flexible blocks. [Polymer, 2015, 80, 245]

We studied the capability of these BCPs, neat or in blend with electron acceptor materials, to arrange into NP dispersions in aqueous medium through miniemulsion without surfactants, exploiting the hydrophilic coil behavior and avoiding expensive purification steps. The chemical nature of the coil block promotes intra- and intermolecular interactions in the neat NPs or those blended with fullerene derivatives, leading to the ideal nano-aggregation morphology for organic solar cell active layers. The relationship between the nano-aggregation of the NPs, their physico-chemical properties, the charge transfer in the blended NPs, and the device performances will be discussed. [Adv Sustainable Syst, 2018, 2, 1700155]

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#050 - Doping strategy of organic semiconductors

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Organic electronics utilize low-cost, solution-processable, and readily tunable semiconducting organic materials in a variety of applications such as LEDs, photovoltaics, thermoelectrics, and transistors. One common way to tune the important electronic properties of this class of materials is through molecular doping, that is, oxidizing or reducing the organic semiconductor to create an appreciable quantity of equilibrium charge carriers. However efficient doping is dominated by various effects that are currently not well understood. Here we report doping strategies adopted for two class of compounds, *n*-type small molecules (naphthalenediimide derivatives) and *p*-type polymer (P3HT), which allows improving their thermoelectric properties. The structural investigation of doped films points out the dependence of thermoelectric performances on the molecular arrangement, which is strictly related with the chemical structure of both the semiconductor and the dopant.

#051 - Porphyrins for photovoltaic applications

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Porphyrins are characterized by strong light-harvesting abilities and chemical, photochemical and thermal stability. Since their energy levels can also be easily tuned by chemical modification, this kind of molecules are a good candidate to be implement in photovoltaic devices.

Push-pull porphyrins featured by a strong internal charge transfer, have reached interesting photon-to-current conversion efficiencies in dye-sensitized solar cells (DSSCs),¹ which best perform in diffuse light conditions² and can be considered as a potential solution for the development of photovoltaic glass, both for the outdoor and the indoor, to be applied in the making of future zero-energy buildings (ZEBs).

However push-pull porphyrins are obtained by multistep synthesis with low overall yields, on the contrary β -functionalized porphyrins offer the possibility of a straightforward synthesis with higher yields, and therefore more adapted for a large scale production.³

Here we will present our recent results in the study of β -substituted porphyrins as dyes in DSSC prototype devices, where the components will be realized by means of different thin-film deposition techniques, such as screen and ink-jet printing.

Finally, we will also present our preliminary results in the implementation of photoactive porphyrin thin layer in hetero-junction photovoltaic cells realized through physical vapor deposition.

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#052 - Large area Photon harvesting from metal-dielectric metasurfaces via bottom-up and laser interference lithography approaches

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Large area Photon harvesting from metal-dielectric metasurfaces via bottom-up and laser interference lithography approaches

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Periodic arrays of metal and metallo-dielectric structures are targeted for the development of optoelectronic components orbiosensors [1, 2] and emerging photovoltaics for their unique properties and functionality based on localized surface plasmon resonance (LSPR). Current top-down approaches of nanoscale fabrication like electron beam lithography or scanning probe lithography are excellent in control of size and shape but suffer serious drawbacks of small area coverage and time consumption. On the other hand, bottom-up approaches like self-assembling methods [4, 5] successfully produce large area patterns but possess less control on array periodicity and ordering. Among bottom-up approaches, defocused ion beam sputtering (IBS) represents an inexpensive and time-saving way to fabricate large-area arrays of self-organized nanopatterns which feature broadband and tunable plasmonic functionalities [4]. In many applications like e.g. in plasmon enhanced sensing, sharper and tunable plasmon resonances are highly desired. In this work, we demonstrate the fabrication via laser interference lithography (LIL) of mono-dispersed arrays of one-dimensional vertically stacked plasmonic nano-structures featuring plasmon hybridization engineering. The metasurfaces feature magnetic dipole resonances in the near infrared part of spectrum associated to strong subradiant near-field enhancement up to a factor of 12 [4]. We compare the results with similar plasmonic nanostructures synthesized by self-organized IBS, demonstrating the role of order in the plasmonic response of such metasurfaces. Large area plasmon enhanced applications are thus foreseen in nanospectroscopies like e.g. Surface Enhanced Raman Scattering and in non-linear applications. Photon harvesting effects have also been demonstrated by realizing ordered sub-wavelength all-dielectric patterns on silica substrates, featuring *moth-eye* antireflective effect: we report a decrease of the reflectance of SiO₂ up to 16% which calls for a successful application on front windows of solar cells.

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#053 - Luminescent solar concentrators based on silicon nanocrystals

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Proposed by Lerner et al.¹ in the 1973, luminescent solar concentrators (LSCs) represent nowadays one of the possible solutions for a sustainable future. LSCs are systems, typically in the form of plates, which convert sun light into electricity by exploitation of the optical phenomenon called total internal reflection (TIR). Luminescent chromophores are embedded inside a transparent waveguide (glass or polymeric one) or deposited above it. Upon solar light excitation the luminescent species emit light that is directed to the edges of the system by TIR, where a photovoltaic cell is placed. This architecture allows the conversion of a certain amount of light into electricity; the remaining part of the solar spectrum passes through the coloured or semi-transparent matrix, opening the way to the building of photovoltaic windows: "Solar Windows".

In this case, silicon nanocrystals (SiNCs) in the quantum size range (diameter=2-12 nm) have been used as a luminescent species, able to absorb in the near UV and emit in the NIR, remaining transparent in the visible spectral region. Compared to more traditional quantum dots, such as CdSe, SiNCs offer several advantages such as the lack of toxicity, the abundance of the main component, the high sustainability and the high Stokes-shift due to the indirect band gap nature.

In this study, solution phase, SiNCs were functionalized with 1- dodecene through a low temperature approach and they were i) embedded in acrylic polymer matrix by thermally initiated bulk co-polymerization, ii) dissolved in a polymeric solution and deposited on a transparent substrate in order to obtain a thin film.

Once the LSC was obtained it was possible to characterize its morphology, its optical and structural properties.

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#054 - Elaboration of p-type emitters on n-type silicon wafers: experimental conditions effect of boron diffusion

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Other Authors: Abdelkader Elamrani, Ali Saibi, Youcef Belkacem, Chahinez Nasraoui

N-type crystalline silicon based solar cells have attracted considerable attention in the recent few years from researchers and solar cells manufacturers due to its high bulk lifetime, as well as to the absence of the light induced degradation lifetime caused by the presence of the boron-oxygen complexes. The elaboration of a p-type emitter on n-type wafer can be performed by several methods, in this work, a paper boron source so-called preform source was used. The main objectives of this study were to investigate the effect of boron diffusion temperature and duration as experimental conditions on the different characteristics of the formed emitter, like sheet resistance, boron surface concentration and depth junction by using four point probe and secondary ion mass spectrometry.

#055 - Ultra-high temperature Ceramic matrix composites for extreme environments*Luca Zoli - CNR-ISTEC**Other Authors: Antonio Vinci (CNR_ISTEC), Pietro Galizia (CNR_ISTEC), Diletta Sciti (CNR_ISTEC).***Ultra-high temperature Ceramic matrix composites for extreme environments**

The impelling demand for materials able to operate at temperature above 2000 °C pushes the scientific research towards continuous search of materials possessing a combination of properties more and more challenging. C/SiC composites are currently the most used materials for aerospace applications, such as nose cones, leading edges and rocket nozzles, owing to their excellent high-temperature strength, high thermal conductivity, low coefficient of thermal expansion, good thermal shock resistance and good ablation resistance but their operational limit is around 1600 °C. Thus the development of a new generation of Ceramic Matrix Composites (CMCs) working at higher temperature is a key goal that could be achieved by combining a chemically and mechanically robust and oxidation resistant matrix with a reinforcing phase, such as CFs. In this context, advanced ceramic materials, boride and carbide of early transition metals, named Ultra-High Temperature Ceramics (UHTCs) may be the right option as the constituent matrix of these new composites.

ISTEC activities have been recently focused on fabrication of Cf/ZrB₂-SiC composites which have the potential to operate above 2000 °C.

This lecture illustrates processing techniques and characterization of UHTCMCs focusing on the aspects of matrix densification, fiber/matrix interface, thermal shock resistance and oxidation behavior.

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#056 - Mechanical behaviour of carbon fibre reinforced carbides up to 2100°C*Antonio Vinci - ISTEC - CNR**Other Authors: Luca Zoli (ISTEC - CNR), Diletta Sciti (ISTEC - CNR), Jeremy Watts (MS&T), Gregory Hilmas (MS&T), W.G. Fahrenholtz (MS&T)*

Ultra-high temperature ceramics (UHTCs), such as the carbides and borides of early transition metals, are a class of materials characterized by very high melting points, high ablation resistance and thermal conductivity and are being considered for the application in extreme environments. The major drawbacks are the low fracture toughness and thermal shock resistance which limit their implementation. Previous studies showed the capability of carbon fibres to improve the damage tolerance of these materials but no high temperature characterization has been carried out. In this study, carbon fibre reinforced TaC/SiC and ZrC/SiC composites were produced by slurry infiltration and hot pressing. SiC was added to both compositions to limit grain growth and aid sintering. The microstructure was analysed by SEM - EDX and X-Ray diffraction and flexural strength was evaluated from room temperature to 2100°C. The microstructure is characterized by the presence of fine carbide grains which did not coarsen during sintering and fibres did not show evident signs of reaction at the interface. The main phases were c-ZrC, c-TaC, h-SiC and graphite from the carbon fibre, but after testing at 2100°C no SiC was detected on the surface. The flexural strength increased from 260 - 300 MPa at room temperature to 450 MPa at 1500°C, which was attributed to stress relaxation. At 1800°C the strength decreased to 410 MPa for both samples. At 2100°C plastic deformation resulted in lower strength at the proportional limit (210 - 320 MPa) but relatively high ultimate strength (370 - 440 MPa). The sample containing ZrC had a lower ultimate strength but higher failure strain at 2100°C due to weak fibre/matrix interface that resulted in fibre-dominated composite behaviour.

#057 - The challenging mechanical characterization of continuous fiber-reinforced ultra-high temperature ceramics for extreme conditions

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Other Authors: Luca Zoli, Antonio Vinci, Simone Failla, Diletta Sciti

Ultra-high temperature ceramic matrix composites (UHTCMCs) are currently attracting an increasing research interest for their potential impact in the aerospace field [1]. Respect to the already used C/SiC composites (as nose cones, leading edges and rocket nozzles), UHTCMCs promise to increase operating limit from ~1600 °C to above 2000 °C. In this talk we highlight the microstructural and chemico-physical features that distinguish novel UHTCMCs from the well-known C/SiC composites, and how those differences should be taken into account in order to set the mechanical tests conditions, and to elaborate the data.

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#058 - Trifunctional device for smart glass applications

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In the last decade industrial research focused its attention on “smart” advanced glasses based on electrochromic (EC) devices. EC glass windows could improve energy efficiency in buildings, with modulated transmittance of light (upon externally applied voltage) and dynamic solar control, enhancing the human comfort of the internal environment and - at the same time - regulating the solar energy transfer through the window, reducing the expense for building heating and cooling.

At the same time, innovative devices that combine organic light emitting diodes (OLEDs) functionality with photovoltaic (PV) response have gained wide interest, as they can generate electricity in the daytime and provide illumination during the night.

In this context, an interesting evolution of smart windows technology is represented by a multifunctional integrated photovoltaic/electrochromic/lighting (PV/EC/OLED) device. In fact, this trifunctional window could act as solar cell module, as self-powered electrochromic smart window able to provide a shading control and as light source during night time, thus creating new market and business opportunities in the field of green energy applications in buildings.

Although the integration of two technologies, OLED/PV or PV/EC has already been proposed, no study has been published on the development of a trifunctional “single glass” device involving energy production (PV), lighting (OLEDs) and solar control (EC) features.

We present an innovative trifunctional device combining: semitransparent perovskite solar cell, solid state EC device and full transparent OLED. PV and EC device are deposited each on one side of the glass, while the OLED is grown on the top of EC device, using a common ITO electrode. The perovskite solar cell was fabricated on sputtered ITO anode by spin-coating. The cathode (Ag) was deposited by thermal evaporation in an ultra-high vacuum chamber. The PV device was designed so as to obtain 3 cells connected in series, in order to reach an adequate voltage to power on the EC device. The latter, positioned on the opposite glass side, consists of an electrochromic film (WO₃) and a solid-state electrolyte (Nafion) sandwiched between two ITO electrodes. The top electrode of EC device acts as anode for the OLED, fabricated on its top by thermal evaporation. The OLED cathode consists of an Ag/WO₃ double layer and the relative thicknesses have been chosen in order to maximize the device transmittance.

#059 - Biomorphic ecoceramics prepared using cork as template agent

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The use of renewable feedstocks in chemical processes is a crucial element for sustainable development, in line with the green chemistry principles. Biomorphic materials are an example of this, as they are materials prepared using a natural template agent, and which maintain the same 3D structure of the natural compound.

Cork, the bark of the of the evergreen oak *Quercus suber* L., is a particularly interesting template agent, due to both its sustainable use (to harvest the bark, the tree is not cut) and its 3D structure (prismatic honeycomb-shaped cells).

In this work we report the preparation of cork-derived ceramics, to be used in biomedicine (i.e. hydroxyapatite Ca₁₀(PO₄)₆(OH)₂) or for environment remediation (i.e. zinc oxide ZnO). Cork was first converted into graphitic carbon through a pyrolysis process; it was then infiltrated with suitable chemical precursor(s) and finally converted into the desired ecoceramic through a calcination at an appropriate temperature.

Results showed that the ecoceramics maintained the same porous 3D structure of the cork; a characterisation of the materials was performed, as well as testing of some functional properties.

#060 - Placing of amino acids in microporous materials: a ZSM-5 and L zeolites Synchrotron x-ray characterization after l-lysine adsorption

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Amino acids, which represent the proteins primary structural unit, belong to an important class of organic compounds exploited in several application fields, such as pharmaceutical, biomedical and food processing industries. The global market based on the amino acids production is constantly growing and cutting-edge sorbent materials for separation processes are continuously required to decrease amino acids losses during adsorption/desorption cycles. Zeolites and their adsorption properties represent an effective material in placing amino acids in form of well ordered-layers on the solid surface (Qiang et al, 2008). Based on this, two samples of l-lysine loaded ZSM-5 (SiO₂/Al₂O₃ ratio (SAR) = 51 and 21, respectively) and one sample of L (SAR 6.1) were characterized through a multidisciplinary approach. Batch method (pH=5.5) was used to enable l-lysine sorption process, capillary electrophoresis separation technique was applied to obtain adsorption isotherms, while thermal analysis were used to quantify the total weight loss. Furthermore, Synchrotron X-ray powder diffraction (carried out at the MCX Beamline of Elettra Synchrotron, at Room Temperature and using a fix wavelength of 0.82700 Å) was performed to study ZSM-5 and L sorption capacity and structural modifications driven l-lysine adsorption. Rietveld structural refinements (processed through the GSAS-EXPGUI software package; Larson and von Dreele, 1994; Toby, 2001) were carried out in monoclinic (s.g. *P2₁/n*) and hexagonal (s.g. *P6/mmm*) symmetry for ZSM-5 and L zeolite, respectively. Results obtained through difference Fourier map analysis highlighted that: in both ZSM-5 samples, l-lysine is located at the intersection of sinusoidal and straight channel and within the sinusoidal channel, while in L zeolite the molecule was detected within the monodimensional channel (*i.e.*, 6 possible orientations). Refined occupancies revealed an amount of extraframework species of about 4.85, 6.51 and 17.63 % for ZSM-5 SAR 51, ZSM-5 SAR 21 and L zeolite, respectively. The content quantified is in good agreement with adsorption isotherms data and thermal analysis results. After l-lysine adsorption, no noteworthy structural deformations were detected: channels retain their circular geometry. All the information gained revealed that ZSM-5 as well as L zeolites are efficient in l-lysine adsorption and this suggests a possible exploitation of both as sorbent materials in biocatalytic processes.

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#061 - Switchable Dynamics and Flexibility in Gas-absorptive Porous Materials

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Our approach is to design porosity in combination with switchable *dynamics and flexibility* in porous materials for gaining control over gas capture and selectivity. This approach was made possible by fabricating rotor-on-axel molecular struts and tetrahedral building blocks.

Ultra-fast molecular rotors as fast as 10^{11} Hz were engineered in porous crystalline frameworks (molecular crystals, MOFs and mesoporous organosilicas) containing rod-like linkers as amphidynamic elements. The porous frameworks promise access to the control of rotary motion by chemical and physical stimuli. If a gas or a vapor is diffused to the cavities, such as CO₂, iodine and hydrocarbon vapors, rotor dynamics is hampered. In turn, on/off switching produces modulated physical responses. When C-F dipoles were mounted on the rotors, they induced fast oscillating dipoles that interact with an applied electric field. Direct evidence of host-guest interactions at the molecular level were established by 2D solid-state NMR.

We achieved the fabrication of swellable porous adamantoid frameworks by the use of highly symmetrical tetrahedral elements and the co-operation of 8 surrounding hydrogen bonds mounted on conformationally flexible groups. The flexibility of the porous crystals manifests itself in response to stimuli of selected gases: CO₂, Xe and hexane triggers the enlargement of channel cross-section. The accomodation of CO₂ and Xe in the channel chambers was revealed by synchrotron-light XRD, combined with modelling. Xenon dynamics was gathered by ¹²⁹Xe NMR chemical shift anisotropy profiles, which encode the shape and orientation of each visited cavity. Jump rate and activation energy experienced by exploring Xe atoms were uniquely established.

Covalent connection of tetrahedral nodes results in expandable frameworks, especially if 3 instead of all 4 branches are cross-linked: the forth branch can be dedicated to bearing a functional group to catch the gas molecules (CO₂ is retained by -NH₂ group by an energy as high as 54 kJ/mol).

Moreover, photo-responsive molecular crystals were fabricated by tetrahedral azobenzene tetramers that form porous molecular crystals in their *trans* configuration. The efficient *trans-to-cis* photoisomerization converts the crystals into a non-porous phase but crystallinity and porosity are restored upon reverse isomerization promoted by heat. We demonstrated that the photo-isomerization enables reversible on/off switching of optical properties as well as CO₂ capture from the gas phase.

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#062 - Dynamics and Stimuli-Responsiveness of Supramolecular Polymers at High Resolution via Molecular Modelling

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Nature, with billions of years at its disposal, has been able to produce materials that express fascinating dynamic properties and complex adaptive functionalities, far superior to what is currently achievable by common technological materials. Learning how to design artificial materials possessing similar properties (self-healingness, adaptivity and stimuli-responsiveness) would be a breakthrough in many fields.¹ However, given the actual experimental limitations in terms of time and length scales, it is extremely difficult to grasp the molecular design rules to control such properties.

Recently, we have combined atomistic and coarse-grained molecular models with advanced sampling techniques to study the self-assembly, the dynamic properties and the stimuli responsiveness of supramolecular materials from a privileged point of view.²⁻⁵ In particular, in a recent work, we investigated the intrinsic dynamics of a benzene-1,3,5-tricarboxamide (BTA) supramolecular polymer in water at remarkably high (sub-molecular) resolution.⁴ Thanks to our approach, we obtained important insights on how the presence of structural defects on the polymer surface can control its intrinsic dynamics and the exchange process with the solution. Then, very recently, we investigated also the dynamic adaptivity and stimuli-responsiveness of this BTA supramolecular polymer via designing simple *in-silico* experiments to get structure-dynamics-property relationships.⁵ The insights we obtained demonstrated that molecular modelling can contribute to open the way toward the rational design of next-generation dynamic materials.

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#063 - LIGHT-POWERED ARTIFICIAL MOLECULAR PUMPS

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LEAPS, "Light Effected autonomous molecular pumps: Towards active transporters and actuating materials" is a research project, funded by an European Research Council Advanced Grant, whose goal is to develop supramolecular systems capable of performing directed and autonomous translational movements activated by light energy and use them for transporting molecular substrates in a variety of set-ups.

The system that we are developing is a pseudorotaxane assembly in which a molecular ring passes unidirectionally through a molecular axle in response to photochemical and chemical stimulation. It is composed of a molecular ring and a non-symmetric molecular axle that comprises: a cyclopentyl unit as passive pseudo-stopper at one end, an ammonium cation as central recognition site for the ring and an azobenzene stopper as bistable photoswitchable unit at the other end.

The ring should enter exclusively from the *E*-azobenzene side of the axle for kinetic reasons, affording a pseudorotaxane in which the macrocycle encircles the recognition site on account of hydrogen-bonding interactions between the oxygen atoms and the ammonium centre and, possibly, π -stacking forces involving the naphthalene and azobenzene units. Subsequently, light irradiation converts the *E*-azobenzene unit into the bulkier *Z* form, a process that causes a destabilization of the supramolecular complex and dethreading of the components.

The next step will be to develop a "second generation pump" by replacing the cyclopentyl pseudostopper with an appropriately substituted phenyl unit, that is easier to functionalize, in order to add further components to the system. Another option is to append an alkyl chain of suitable length at the pseudostopper side, which can act as a reservoir for collecting molecular rings, pumped by light. A nanodevice of this kind is of high interest because it would convert the energy of the incident photons into chemical energy in the form of molecular rings stored under a non-equilibrium condition.

#064 - Chirality in mechanically interlocked molecules

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Since the observation of optical activity in sodium ammonium tartrate crystals by Pasteur, chirality has played a central role in the development of the theories of chemical structures. The initially observed point chirality, arising from tetrasubstituted carbon atoms, has then been expanded to encompass axial, planar, and helical stereogenic elements. With the advent of the mechanical bond, the playground for the preparation of novel chiral molecules has largely expanded. In particular, mechanically interlocked molecules (MIMs) can potentially display chirality arising directly from the mechanical bond. However, this field still remains relatively poorly explored.

We recently undertook the investigation of a palindromic symmetric rotaxane where pH variations can be used to enable shuttling of a crown ether macrocycle between two identical triazolium stations. Depending on the substitution pattern of the macrocycle, upon deprotonation of the central ammonium station, two enantiomers can be generated. Furthermore, the enantiomers can interconvert thanks to the ring shuttling equilibrium. Therefore, thanks to the mechanical bond, such system can potentially reversibly switch between three states: symmetric/prochiral, and the two separate enantiomers, which is unprecedented in supramolecular chemistry.

#065 - Azacryptands as receptors for anions on solid supports and nanomaterials

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Molecular cages, bistren cryptands and cryptates in particular, are well-known versatile receptors for anion inclusion in water. Macrobicycles can be easily synthesized through the Schiff base condensation of tren with the chosen dialdehyde, followed by the hydrogenation of the six imine bonds. The ellipsoidal cavity of the cage can be varied at will, by choosing the appropriate dialdehyde, in order to include substrates of varying sizes and shapes. Our group recently demonstrated that, by opportunely mixing different spacers linking the tren units, new cages can be obtained with improved capabilities, e.g. in terms of selectivity, to be applied as effective anion receptors and sensors. We have now improved the synthetic strategy, and prepared new sophisticated asymmetric cages

(i) to be applied as multi-channel sensors for anions, or (ii) to be incorporated in new (nano)materials (e.g. gold nanoparticles, glass, silica). In case of the multi-channel sensors (i), the cage systems have been designed in order to give a multiple response to the bound anions. To this purpose, the new systems display multiple responsive groups (e.g. two different fluorophores). The obtained selective receptors are proved to give a different spectroscopic response (i.e. signal), according to the nature of bound anionic guest. Asymmetric cryptates have been also successfully (ii) immobilized on gold nanoparticles, opening new perspectives in the development of materials, based on selective cage receptors for the selective extraction, recovery from water, and sensing of anionic pollutants.

#066 - Supramolecular Hydrogels based on Low-Molecular-Weight Gelators: preparation and applications

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Supramolecular Hydrogels based on Low-Molecular-Weight Gelators: preparation and applications

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Low-molecular-weight gelators (LMWGs) are receiving great interest because of their capability to form functional gels in a very simple and sustainable way.

The formation of gels arises from the self-assembly of these small molecules into long structures (most commonly fibers) thanks to weak interactions like hydrogen bonds and π - π stacking. These fibers entangle, leading to networks able to immobilize the solvent.

Several methods have been recently developed as trigger of the gelation process of LMWG molecules, such as temperature variation, ultrasound sonication, salts addition, pH change, dissolution in solvent mixtures, light irradiation, or amino acids addition.

These gels differ from permanently covalently cross-linked polymers gels because the cross-linking can be reversed by an energy input, for example by heating [1].

LMWGs, despite their small size, closely mimic biomacromolecules and are often biocompatible. Moreover, it is possible to tailor these molecules to obtain different materials, suitable for several applications, from regenerative medicine (3D cells culture, drug delivery, etc.), to environmental pollution remediation (water pollutant adsorption and photo-degradation), or biomineralization (influence on crystal nucleation and growth).

Recently, we focused our attention on the synthesis of two hydrogelators with different uses.

The first one, a Tyrosine-Oxazolidinone based LMWG [2], was used to prepare transparent hydrogels containing TiO₂ nanoparticles (NPs) and TiO₂-NPs/graphene composites, for application in the photodegradation of a model pollutant compound (Rhodamine B) upon UV irradiation [3].

The second, a L-DOPA (L-3,4-dihydroxyphenylalanine) based LMWG, can form strong hydrogels with neutral final pH. It was used as scaffold for the controlled nucleation and growth of calcium carbonate crystals for studies in the biomineralization field. The obtained organic/inorganic composite materials were characterized from rheological, mineralogical and morphological point of view.

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#067 - A Self-assembling Peptide Hydrogel for Ultrarapid 3D Immunoassays

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Diagnostic array platforms rely on the intimate structure-function relation of immobilized probes. In this context, hydrogels are appealing semi-wet systems to locally confine biomolecules while preserving their structural integrity and function. Yet, limitations on biomolecule diffusion rates or fabrication difficulties have hampered their broad application. Here, using micromolar concentrations of a self-assembling peptide, a printable and self-adhesive hydrogel was obtained and applied to the 3D immobilization of biomolecules on analytical slides. This soft matrix represents a robust and versatile material allowing selective tuning of analytes diffusion, that is here exploited to run in-gel immunoassays under solution-like conditions in an unprecedented (<10 min) time frame. The developed material overcomes major limitations associated to hydrogel for immunoassays, widening the perspectives of easy fabrication of multifunctional bio-interfaces for high-throughput, molecular recognition assays.

#068 - Fluorescence transduction of host-guest complexation in solution

Pasquale Pagliusi - Università della Calabria

Environmental chemical sensing needs stringent sensor requirements in terms of sensitivity, selectivity and ruggedness. The use of molecular receptors as sensing materials is particularly attractive to address the selectivity issue, exploiting the concepts of shape recognition and binding site complementarity. In the last decades, several groups have approached sensing of organic molecules with molecular receptors, mainly using cyclodextrins, calixarenes and cavitands. Among them, conformationally blocked quinoxaline-based cavitands (i.e., MeQxBox, EtQxBox) have been recently proposed to enhance the complexation strength toward aromatic VOCs.

On the other hand, effective transduction modes for the molecular recognition event is also required for highly consistent and sensitive detectors. In this context, photoluminescence is one of the most versatile and sensitive techniques for the detection of chemical species in solution, and for this reason standard UV–VIS–NIR spectrofluorimeters, easy to use and low-cost instruments, are largely employed in research and analytical laboratories.

Exploiting the intrinsic photoluminescence of the EtQxBox, here we report a combined steady-state and time-resolved fluorescence investigation aimed at assessing the complexation capability of EtQxBox in solution toward aromatic and aliphatic VOCs. Quantitative estimation of the dynamic and association constants for benzonitrile and acetonitrile confirms the high selectivity of EtQxBox toward aromatics. Nonetheless, aspecific collisional quenching coexists, making steady-state-only fluorescence transduction mode prone to false positives in presence of aliphatic interferents

#069 - Printed Organic Transistors for High-Frequency and Edible Electronics*Mario Caironi (I) - Istituto Italiano di Tecnologia*

Printed organic field-effect transistors (OFETs) have been considered for many novel applications towards large area and flexible electronics, since they can enable pervasive integration of electronic functionalities in all sorts of appliances, their portability and wearability. However, printed OFETs fabricated with scalable tools fail to achieve the minimum speed required for example to drive high-resolution displays or to read the signal from a real-time imager, where a transition frequency (f_T), i.e. the highest device operative frequency, above 10 MHz is required. In this seminar I will present effective strategies which I have been developing with my team with the ERC project "HEROIC" to increase f_T of polymer devices up to tens of MHz by combining only printing and laser-based direct-writing techniques.

A further inspiring opportunity of organic semiconductors stems from the use of natural or bioinspired materials to develop edible electronic systems, composed of devices that can be safely ingested. Ingestible electronics could potentially target a significant number of biomedical applications, such as monitoring patients' compliance to medications, and of applications in the food packaging as well, by providing ingestible smart tagging of perishable goods. Here I will report on a recent approach we have developed towards ingestible electronics integrated into food and onto pharmaceutical capsules. The approach relies on the printing of bio-compatible OFETs on commercial, temporary tattoo-paper, and on the transferring of conformable, ultra-thin active electronic elements onto edible substrates, with a process as simple as children's use of temporary tattoos.

#070 - Terahertz radiation transport regimes in three-dimensional disordered media*Silvia Gentilini - ISC-CNR*

Other Authors: Claudio Conti (ISC-CNR, Physics Dep. University "La Sapienza") Neda Ghofraniha (ISC-CNR) Mauro Missori (ISC-CNR)

The propagation of electromagnetic (EM) waves in random media is a topic of considerable interest in many research fields since it can lead to a plethora of phenomena. With respect to standard techniques in the visible range, the detection technology available in the THz spectral range provides the advantage to easily access the amplitude and the phase of the EM field. We report the measurements of the electric field transmitted by media with a 3D disorder, obtained by means of THz time-domain spectroscopy.

We report the measurements of the electric field transmitted by media with a three-dimensional disorder, obtained by means of THz time-domain spectroscopy. The samples are made by dispersions of 1 mm diameter Silica spheres in a Paraffin matrix with refractive index 1.95 and 1.5 respectively, prepared at filling fraction, ν , ranging from 0.05 to 0.5. These dispersions are then solidified in cylindrical molds with 15mm diameters and variable thickness L ranging between 2 to 16mm. We collected the temporal signal $E(t)$ transmitted by the sample over 800 ps at different filling fractions. By taking the Fourier transform of these signals, we can extract the spectral amplitude, $E(\omega)$, and phase, $\varphi(\omega)$, in a frequency range between 0.2 and 2 THz. The objective of our measurements is to unveil signatures of transition of the photons transport regime.

The first set of measurements, performed on the 16 mm thick samples and varying the filling fraction, shows that at low filling fractions, the spectral amplitude $E(\omega)$ displays resonances attributable to the Mie scattering. Such resonant behavior is gradually washed out by the increasing de-coherence effect introduced by the increasing number of scatterers. In order to provide a dynamic observable able to quantitatively characterize the photon transport regime, we estimate the group delay $\tau_g = d[\varphi(\omega)]/d\omega$. We compare τ_g with the phase delay τ_p obtained as the ratio between the speed of light and the mean refractive index of the samples. The discrepancy between τ_g and τ_p increases for $\nu > 0.1$ denoting a transition from a ballistic to a diffusive transport regime. At $\nu > 0.25$, τ_g reaches a plateau, signature of the onset of photon trapping mechanism.

The second set of measurements was obtained by varying the thickness of the samples for three volume fractions ($\nu = 0.05, 0.2$ and 0.4) corresponding to the propagation regimes previously identified. We calculated the transmission T by integrating the spectral amplitude, $E(\omega)$, on different spectral intervals. We found that for low frequencies (0.2-0.5 THz), a crossover in the behavior of T vs L is observed with the increase of the filling fraction. Specifically, for $\nu = 0.05$ and 0.2 the curves display a power law behavior in agreement with a diffusive regime; the curve, for $\nu = 0.4$, exhibits an exponential trend, as expected when the localization of EM field takes place in a strongly scattering medium.

#071 - Charge transport mechanisms in small molecule:polymer blend organic field-effect transistors*Alberto Scaccabarozzi - Istituto Italiano di Tecnologia*

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Organic electronics have attracted considerable interest over the last decades promising an alternative to conventional, inorganic electronics platforms. The extensive research in the field led to great advances in the understanding of charge transport mechanisms of organic materials and remarkable enhancement of field-effect transistors (OFETs) charge carrier mobilities, which exceeded the

benchmark value of $10 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$.¹⁻³ Among other materials, small molecules demonstrated outstanding charge transport properties due to their highly ordered crystalline microstructure, however they lack of the easy processability typical of polymers. The latter are indeed easily cast in thin films with industrially scalable solution based printing techniques, in spite of lower charge carrier mobilities. To fully exploit the touted potential of organic materials, a promising solution is represented by the employment of multicomponent systems in which polymer and small molecules are blended together. Different examples have been reported exploiting this strategy leading to the production of high mobility OFETs.¹ Despite it looks clear that optimal morphologies of these blends can lead to noticeable enhancement of charge carrier mobility when compared to their neat materials counterparts cast from solution, the charge transport mechanism is still somehow uncertain.

In this work we employ a blend system comprising the 2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C₈-BTBT) small molecule, the indacenodithiophene-benzothiadiazole (C₁₆IDT-BT) polymer, with the addition of a fullerene based molecular dopant, C₆₀F₄₈, which has been reported showing a hole mobility exceeding $13 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$.¹ We investigate the charge transport mechanisms of this blend showing that despite a negative mobility-temperature dependence, which could be a hint of band-like transport, the polymer is active in the charge transport and it does not simply act as a filler. We employ an optical spectroscopy technique, charge modulation spectroscopy (CMS), to show the characteristic polaronic absorptions and bleaching features of IDTBT and BTBT induced by the accumulated charge carriers in the blend device. The contributions of semiconducting polymer, small molecule and dopant to the charge transport is clarified by coupling CMS with a confocal scanning microscope and mapping the charge carrier distribution.

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#072 - Flexible, real time and direct ionizing radiation detectors based on high mobility amorphous oxide thin film transistors

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Large-scale ionizing radiation dosimetry is crucial in diverse areas such as nuclear waste management, radiotherapy or personal protection devices. Most current sensitive wearable dosimeters employ an optical readout after exposure and do not provide real-time information. Here we present novel Radiation sensitive Oxide semiconductor Field-Effect Transistors (ROXFET) that are based on high mobility semiconducting oxides and a multilayer dielectric formed by SiO₂ and Ta₂O₅. This kind of structure provides real-time X and gamma ray direct detection at room-temperature. Our measurements demonstrate that the absorption of the high-energy photons causes the accumulation of positive ionization charges into the multilayer dielectric of the device and the consequently shift in threshold voltage of up to 3.4 V/Gy. The mechanism of detection is based on the well-known CMOS RADFET concept, but the novelty of the materials and structures that we implemented improved this technology in terms of sensitivity, portability and readout system. First of all the high-Z Ta₂O₅ increases the cross section of interaction between the photons and the active layer making possible to achieve sensitivities one order of magnitude greater than the standard RADFET ones. Besides, amorphous oxide materials are processable at low temperature (<150 °C) allowing the fabrication of flexible and large area devices onto plastic and low cost substrates. Finally, high mobility combined with a steep sub-threshold slope of the transistor allow fast and ultra-low power readout of the deposited radiation dose. Moreover, the observed order of magnitude variation in the transistor channel impedance due to the ionizing radiation makes it possible the integration of the detector into a fully passive, wireless and real-time system of readout based on a RFID sensor tag. In this way we achieved a flexible, passive, programmable, wireless sensor that reports in real-time the excess of critical high-energy radiation doses.

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#073 - Towards the Fabrication of Flexible Organic Thermoelectric Generators

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Nowadays, micro-thermoelectric generators based on thin film of Bi₂Te₃ demonstrate the reliability and commerciality of the thermoelectric technology.[1] The requirements of both sustainability and large-scale production made organic thermoelectric

generators (OTEG) gaining high attention within the thermoelectric community as based for a novel class of modules. In fact, OTEGs not only represent the alternative to the present metal-compound thermoelectric devices, but also fulfil prerequisites that the present technology does not satisfy, allowing the fabrication of flexible and lightweight modules implementable where adaptability to curved and irregular surfaces, and to surfaces changing in motion is needed. Moreover, flexibility results in easier adaptability of the devices, and therefore lower integration costs.

This project has the objective to fabricate thin-film OTEGs based on conjugated polymers by inkjet printing method. This manufacturing non-contact technique is suitable for low-cost and large-area fabrication of flexible organic devices.[2] Here, we report the state-of-art of our research on both the screening and assessment of efficient and air-stable p- and n-type thermoelectric organic materials, and on the first OTEGs proof-of-concept. The materials and the devices are tested in homemade custom setups for the thermoelectric measurements.[3,4] The most efficient thermoelectric materials were then developed as ink for the printing technique, forming the legs of the thermoelectric generators during the fabrication process.

Moreover, in collaboration with the Smart Materials Lab (@IIT Genova), cotton fiber based materials were functionalized using both carbon nanofibers and graphene nanoplatelets. Here, we report the measurements of the thermoelectric properties of these new interesting kind of materials as a function of temperature and of different parameters.

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#074 - Use of CVD-Graphene as electrodes in nanometric channel n-type Organic-Field-Effect-Transistors

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Despite considerable advances in understanding and controlling the fundamental mechanisms, several bottlenecks still restrict the miniaturization of Organic Field Effect Transistors (OFETs) towards the nanometric scale. In short-channel architectures, charge transport is often dominated by non-linear Space Charge Limited Current (SCLC) while drain-induced-barrier lowering manifests in high off-state currents.

In this scenario, careful choice of materials or chemical treatment of contact electrodes, and more in general of the overall device architecture, are needed in order to optimize the OFET response at nanometric scales. At this regard, graphene has been recently considered as a novel electrode material in organic field-effect devices, taking advantages from their work function tunability, permeability to the transversal electric field and overall chemical stability.

In this contribution, we report on the use of CVD-graphene as electrode material in nanometric channel n-type Organic Field Effect Transistors (OFETs) based on thermally evaporated thin films of the perylene-3,4,9,10-tetracarboxylic acid diimide derivatives (PDI-CN₂ and PDI8-CN₂).

We firstly explored the electrical response of nano devices with standard bottom-contact/ distributed bottom gate architecture.

By a thorough comparison with short channel transistors made with gold electrodes, output characteristics of the graphene-based devices suggests that SCLC contribution is suppressed. Moreover, current on/off ratios independent of the channel length (L) and enhanced response for high longitudinal biases are demonstrated for (L) down to 140 nm. Despite the results, a proper output saturation of the currents, in such architecture, is not achieved due to the relatively thick gate dielectric (300 nm, $\epsilon_r=3.9$).

Further advances have been reached by the use of a proper device architecture for nano devices with patterned local gate tracks and an ultra-thin films (8nm) of Hafnium Dioxide as gate dielectric ($C_{HfO_2} \approx 2 \mu\text{F}/\text{cm}^2$). The largely improved gate modulation results in a proper output currents saturation for channel length down to 200nm, with supply biases of few volts.

Through impedance spectroscopy, overlap capacitances and the overall AC response of CVD-graphene electrodes have been investigated as well.

The contribution of the quantum capacitance in the graphene electrodes is clearly observable in terms of capacity modulation with a distinct "V" shape, reaching a minimum value in the vicinity of the Dirac point, and an average modulation of about $2 \text{ fF}/\mu\text{m}^2$. The cut-off frequency of the nanodevice can be thus indirectly evaluated considering the DC transconductance and the measured overlap capacitance of the graphene electrodes. Cut-off frequencies of the order of 10^5 Hz has been obtained for channel lengths of 200nm.

#075 - Challenging strategies towards the industrialization of Perovskite PV technology

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Recently, the perovskite solar cells (PSCs) opened new opportunities for the development of cost-effective thin-film photovoltaic technology, reaching a power conversion efficiency (PCE) record up to 22%. Although many efforts have been made in order to enhance the photovoltaic performance, challenging issues concerning the up-scaling process and stability retard the exploitation of the PSC technology at the industrial level. This presentation will focus on the development of a scalable and cost-effective realization process for the module production. The aim of this action is the correlation between efficiency, scalability and stability that result as crucial hot topics in PSC technology. Both planar and mesoscopic architectures will be discussed with respect the PV performance, the manufacturing flow and the experiment cost.

Furthermore, we discuss about the challenges on the development and characterization of perovskite solar modules. In particular, we report on the state of art of the PV performance for modules on a substrate area of $10 \times 10 \text{ cm}^2$. The main topic is the optimization of the perovskite and the ETL/HTL layers deposited by solution processing. Morphology and thickness of the layers and its interfaces are challenging issues to reach high PV performance.

Finally, we discuss about the main degradation factors which represent the main bottlenecks for the industrialization of PSC technology. We report the results of accelerated lifetime tests obtained on our devices with the optimization of the constituent layers towards a efficient, stable and low cost PV device.

#076 - Structural characterization of TiO₂ gig-lox sponges by Coherent X-ray Diffraction Imaging

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The use of nanostructured materials is representing a breakthrough in many fields of applications owing to their empowered functionalities. In this framework, spongy TiO₂ layers^{[i],[ii]} are deposited by a novel method based on grazing-incidence reactive sputtering assisted by local oxidation. Our material gains porosity, stability and infiltration capability superior if compared to conventionally sputtered TiO₂ layers. The TiO₂ layer is tested as a scaffold for Perovskite Solar Cells, by the capillary infiltration of solution processed CH₃NH₃PbI₃, which allowed reaching efficiency of 11.7%¹. Coherent X-ray diffraction imaging (CXDI) is a novel full-field imaging technique allowing tomographic reconstructions at very high resolution ^{[iii],[iv]}. Here we use CXDI to see at the mesoscale in 3D how the solution infiltrates the TiO₂ matrix and degrades when exposed to air. This example illustrates the potential of CXDI with the next advent of the Extremely Brilliant Source at ESRF promising a 100-fold increase in brilliance and therefore 100 times more intense coherent beams. This spectacular improvement in coherent flux will allow tomographic reconstructions with unprecedented spatial resolution down to 10 nm and tracking temporal structural transformations at the nanoscale on samples as large as 10 μm.

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#077 - Element-specific photoexcitation channels in V-doped TiO₂ photocatalyst: high resolution x-ray spectroscopy.

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Incorporation of dopants in semiconductors is commonly used to modify the optical response and improve the efficiency of related devices. A physical understanding with elemental and local sensitivity of the electron excitation and trapping channels which follow photoexcitation is a prerequisite for knowledge-based materials design. We have deposited V-doped TiO₂ nanoparticles by gas phase condensation which exhibit both photocatalytic activity for -NO₂ reduction and photoelectrochemical water splitting in the visible spectral range $\lambda > 450$ nm, where undoped TiO₂ nanoparticles are completely inactive (1, 2). By using high-resolution x-ray absorption methods (3, 4) using the ID26 beamline at ESRF we show that sub-bandgap visible light absorption is predominantly due to excitation of electrons from V ions to defective and long-lived Ti sites. We thus identify an element-specific photoexcitation channel.

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#078 - Charge carrier dynamics and visible light photocatalysis in vanadium-doped TiO₂ nanoparticles

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A widely investigated strategy to shift the optical absorption and photocatalytic activity of TiO₂ towards the visible light range is doping with ionic species. In this work, we investigate vanadium-doped TiO₂ nanoparticles (V-TiO₂ NPs) with a V/Ti ratio of 3.0 at. % prepared by gas-phase condensation and subsequent oxidation at elevated temperature. V-doping induces both photocatalytic activity for -NO₂ reduction and photoelectrochemical water splitting in the visible spectral range at wavelengths greater than 450 nm, where undoped TiO₂ NPs are completely inactive. The photocatalytic properties are correlated with the ultrafast dynamics of the photoexcited charge carriers studied by femtosecond transient absorption (TA) spectroscopy with three different excitation wavelengths of 330, 400, and 530 nm. Only in V-doped NPs, the photoexcitation of electrons into the conduction band by sub-bandgap irradiation (530 nm) is detected by TA spectroscopy. This observation is ascribed to electronic transitions from an intra-gap level localized on V⁴⁺ cations. The photoexcited electrons subsequently relax, with characteristic times of 200-500 ps depending on excitation wavelength, into Ti-related surface traps that possess suitable energy to promote -NO₂ reduction. The photoexcited holes migrate to long-lived surface traps that have a sufficient overpotential for the oxidization of both 2-propanol and water. On the basis of TA spectroscopy and photocurrent measurements, the position of the dopant-induced intra-gap level was estimated as 2.2 eV below the conduction band minimum.

#079 - Structural stability and electrical resistivity of Nb-doped TiO₂ films prepared by high deposition rate DC-magnetron sputtering

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Nb-doped anatase TiO₂ is a viable candidate for replacing tin-doped indium oxide (ITO), and fluorine-doped tin-oxide (FTO) as a transparent electrode in several technological applications like: flat panel displays, thin film amorphous silicon solar cells or dye sensitized solar cells (i.e. Grätzel cells).

We have produced Nb-doped anatase TiO₂ films (TNO) at high deposition rate (tens of nm per minute) by reactive DC magnetron sputtering from metal targets. High deposition rate is obtained by an active control of the oxygen gas flow in order to stabilize the impedance of the plasma discharge. Film microstructure and preferential orientation of the crystallites are controlled by the total working pressure.

The resistivity of the films is strongly reduced (10^{-3} Ω cm range) by a heat treatment (450-600 °C) in reductive atmosphere (high vacuum). The heat treatment produces a de-oxidation of the Nb-doped TiO₂ films.

The exposure of the films to ambient condition, has been found to play a crucial role in determining the resistivity of the material. In particular, air exposure in the tens of hours range has a dramatic effect on the film resistance. The resistivity of the film increases by one order of magnitude or more, depending on the thickness of the film, with a power-law behaviour.

In order to understand the increasing of the electrical resistivity, TNOs were studied from chemical and structural point of view.

X-ray Photoelectron Spectroscopy (XPS) analysis showed a re-oxidation of the surface of films after ambient exposure. However the cathodoluminescence (CL) measurements revealed that the stoichiometry of the films in the bulk was not changed upon air exposure. These data demonstrated that re-oxidation takes places in the first surface layers of the films and therefore the resistivity of the films do not substantially increase upon re-oxidation.

After air exposure, scanning electron microscope (SEM) imaging revealed the presence of fractures, which extend through the whole films thickness. The number and size of the fractures are related to the films structure and exposure time of TNO in environmental condition.

Oxygen uptake from ambient air is confined to a shallow surface region. It is possible that this mechanism triggers the formation/propagation of the fractures that predominantly contribute to the increase in film resistivity.

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#080 - Molecular Imprinting Technology and solar cells

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Molecular Imprinting Technology (MIT) is applied into a lot of different research and application areas. The technique assures an high selectivity versus target molecule and is therefore used in high performance sensors, chromatographic application and in the pre-treatment process of liquid and gas media. A particular class of these materials called Molecular Imprinting Polymers (MIPs) can be easily synthesized by a low cost and environmental friendly processes. In this work, an application of MIPs materials as counter-electrode in "Platinum free" Dye-Sensitized Solar Cells (DSCs) was introduced to enhance the selectivity towards triiodide molecule contained in the electrolyte. The latter is commonly a complex matrix containing other than triiodide (the target molecule) also other compounds used as additives and stabilizers that can interfere with the triiodide reduction lowering the cell efficiency. Polypyrrole was

used as MIP and was prepared by electrochemical method. Two different template molecules were used to demonstrate the positive effect of MIP on catalytic activity at the counter-electrode. The influence of different concentration of suitable template on the electrochemical and catalytic properties of PPy on triiodide reduction was studied. The application of MIPs counter-electrode allowed a definite increase in the photovoltaic efficiency of the device as a consequence of the lowering charge transfer resistance at the counter-electrode side related to the triiodide reduction reaction. These results open the possibility for the first time to apply MIP materials into energy systems based on photoelectrochemical cell improving their properties.

#081 - Composition-dependent degradation of hybrid and inorganic lead perovskites in ambient conditions.

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In recent times, halide perovskites have attracted the attention of the scientific community because of their semiconducting properties, low cost, and easy synthesis methods that makes them suitable for applications such as solar cells. On the other hand, these materials are subjected to chemical and structural degradation with consequent performance decrease. In this paper, we investigated the stability of different bromine-based perovskites; hybrid, MAPbBr₃ (MA: NH₃CH₃⁺) and inorganic, CsPbBr₃ and RbPbBr₃. The samples were prepared via single-step solution synthesis as thin films on Au/Pd coated glass substrates and the degradation process was carried out in a climatic chamber at 50 °C and 75 %RH humidity. The structural and chemical evolution of the perovskites were evaluated as function of the exposure time by means of AFM, and AR-XPS, while their optoelectronic properties were monitored by indirect bandgap measurement.

#082 - INVITED TALK: Nature inspires smart materials for tissue regeneration

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New approaches for tissue regeneration aim to recover the original tissue functionality, particularly related to degenerative pathologies affecting bone and osteochondral tissues. Advances in this field are strictly related to progress in materials science aiming to develop new smart bio-devices able to instruct cells with chemical-physical, structural and morphological signals. Biomineralization and biomorphic transformation processes are relevant examples of new nano-technological approaches to obtain nanostructured and nanocrystalline materials in the 3-D state, which is a great challenge to obtain porous scaffolds retaining physico-chemical-mechanical cues relevant for activation of the correct cascade of biological events that lead to tissue regeneration. In fact, thermal consolidation of bioceramics destroys the bioactivity and bio-resorbability of nanocrystalline, multi-doped apatite (HA). Biomineralization process induces and directs the self-assembling of collagen by pH variation, and the simultaneous mineralization with quasi-amorphous apatite crystals, occurring under several control mechanisms exerted by the collagen macromolecule. The process generates hybrid bone scaffolds with high mimicry of osteochondral regions and showing excellent regeneration of critical tissue defects, demonstrated in several preclinical and clinical studies. Biomorphing transformation process consists in a sequence of heterogeneous reactions at the interface between a natural porous template and a reactive gas, generating a highly reactive precursor which can then be transformed into 3-D biomimetic apatite with excellent bioactivity and damage-tolerant mechanical performance. Implementation of these smart materials with remote magnetic activation is made possible by controlled substitution of Ca^{2+} ions with $\text{Fe}^{2+/3+}$ ions in the HA structure, to obtain a superparamagnetic, bioactive and bioresorbable apatite phase (Fe-HA). These magnetic devices, either as nanoparticle or as bioactive hybrid scaffold, are capable of remote magnetic activation and controlled delivery of bioactive factors. New biocompatible guiding systems for cells can be established by enabling selective internalization of Fe-HA by mesenchymal cells and magnetic guiding. The use of nature-inspired synthesis approaches is an elective way to generate smart scaffolds with innate cell-instruction ability, fueling new improved and personalized therapies for tissue regeneration.

#083 - Keratin-based sensors

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We have developed a whole keratin-based ionic sensor for innovative applications in bioelectronics. Electrode integration in keratin thin-film systems allow to study the biopolymer electrical properties for the first time. Reversible binding and extraction of ions from the sensor volume was observed using cyclic voltammetry outperformed inside an environmental chamber with controlled relative humidity (RH) monitored with a traceable hygrometer. Pure keratin acts as an active proton conductor based on proton hopping mechanism and can be chemically doped according to the functionalities that the biopolymer has to fulfill. The addition of glutaraldehyde to the pristine chemical recipe leads to the insolubility of the keratin active layer which can be then exposed to highly humid environment such as, for example, the oral cavity or cell culture to monitor acidity/basicity or ion exchanges. We also added glycerol to increase the mechanical stability of the pure keratin in order to implement the doped biopolymer as a bendable, biocompatible and transparent substrate. Further, we explored the possibility to develop a composite with higher proton conductivity by adding another biopolymer as melanin. Palladium electrodes passivated with hydrogen (PdHx), namely, protodes, were integrated into the sensor architecture to efficiently extract/inject protons and create a reliable amperometric output signal through the ion-sensitive active layer. We report each step of the technological process that led to the engineering of an array of whole keratin-based protonic sensors and every step is supported by experimental data based on cyclic voltammetry, electrochemical impedance spectroscopy and dielectric relaxation spectroscopy (DRS). The optimized insoluble keratin-based sensor showed an ion mobility at RH 80% equal to 0.1 uS/cm^2 , and practical bending properties that can pave the way towards bioelectronics applications where biocompatibility is essential.

#084 - Nature-inspired Biomaterial Instructs Cells Behaviour: 3D Microenvironmental Interaction Between Mesenchymal Stem Cells And Endothelial Cells explored In Bioreactor

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INTRODUCTION

An emerging concept in material science is to draw inspiration from natural processes and products, which we may consider as the most advanced examples of smart nanotechnology. Natural structures such as woods and plants exhibit multi-scale hierarchic organization that is the source of smart and anisotropic mechanical properties associated with high porosity and lightness. Porous woods (rattan) were recently transformed into hydroxyapatite (HA) scaffolds with hierarchic organization focusing on long bone critical defect.

EXPERIMENTAL METHODS

The whole chemical conversion of rattan wood has been carried out through five steps from native wood to porous HA¹. HA-based scaffolds, already commercially available as a biomimetic bone graft were used as control group.

Human adipose-derived mesenchymal stem cells (ADMSCs) were cultured on the 3D samples in birectional perfusion conditions in combination with human umbilical vein endothelial cells (HUVEC) up to 4 weeks in a perfusion bioreactor system (Cellec Biotek AG). Cell viability, cell morphology, protein and gene expression profile were analyzed.

RESULTS AND DISCUSSION

A very high ratio of viable cells was seen with no significant differences between the innovative scaffold and the commercial sample. Microvessels within the 3D microenvironment were detected. The morphological analysis showed ADMSCs grown into the porous scaffold structure remaining firmly attached to the samples surface. The investigation of the expression of proteins and genes involved in the osteogenic differentiation highlighted a significant effect of the bioinspired sample on the up-regulation of the genes involved in both early and late stages of osteogenic commitment if compared to commercial sample.

CONCLUSION

This study demonstrated that 3D scaffold obtained by biomorphic transformation, with already proved high mechanical performance, strongly enhanced the interaction between endothelial cells and mesenchymal stem cells. This achievement is pivotal for a closer mimicry of the complex 3D bone structure and composition which can drive and direct the regenerative cascade at the cell level, towards the regeneration of extensive load-bearing bone parts.

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#085 - Novel multi-doped hydroxyapatite ceramics obtained with CO₂ flux and low-temperature sintering

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A key target of biomaterials research is the preparation of ion-doped hydroxyapatite in the form of 3-D consolidated scaffolds. Apatites doped with various ions such as Mg, CO₃ and Sr are elective biomaterials and relevant drivers of bone regeneration and other properties such as anti-osteoporotic or anti-infective. Doping ions provide apatite with specific biologic functions such as anti-osteoporotic and anti-infective ability; however conventional thermal consolidation processes result in phase degradation into secondary calcium phosphates and elimination of carbonate ions from the apatite lattice, which are main responsible of the apatite bio-solubility. Therefore, the establishment of low temperature, and effective, sintering processes is highly desired. Thermal treatment in CO₂ atmosphere showed to prevent complete decarbonation of apatite phase. In this work, multi-doped carbonated hydroxyapatite is subjected to sintering in CO₂ atmosphere (dry or wet) under controlled gas pressure to achieve solid ceramics with superior bioactivity^{1,2}.

Pure low-crystallinity HA nanopowders with Ca and PO₄ ions partially co-substituted with CO₃, Mg²⁺, Sr²⁺, Zn²⁺ doping ions in different extent were obtained. The XRD analysis of the as prepared multi-doped HA powder, revealed no secondary phases besides the apatitic phase. The TG analysis of the multi-doped HA powders detected CO₂ loss, reporting to a carbonate amount of about 9 wt.% in the starting CHA powder. As per the dilatometry tests, a sintering step in the range 750-900 °C for 1h under flowing carbon dioxide was successful to prevent the carbonate loss from the material, avoiding secondary phases formation and assuring the densification of the samples. The compressive strength and Young's modulus, determined by testing cylindrical specimens (diameter = 9 mm, height = 17 mm), in dense and 80 vol% porous bodies (dense: 543±32 MPa; porous: 6.0±0.5 MPa) resulted twice higher than that found for analogous samples prepared with stoichiometric HA (dense: 308±29 MPa; porous: 3.1±0.3 MPa). Cell seeding was carried out to assess activity, proliferation and differentiation into bone cells that is correlated to different ceramic compositions. Enhanced osteogenic ability was detected in multi-doped apatites in comparison with stoichiometric.

The use of controlled atmospheric conditions is relevant to achieve multi-doped apatite consolidation by low temperature treatments, whereas preventing segregation of the foreign ions and retaining CO₃²⁻ in the apatite structure, with maintenance of small grain size. Such feature is a key aspect to raise the specific surface of the material, to enhance biosolubility and to yield enhanced mechanical strength in dense bodies and porous apatite scaffolds.

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#086 - Ti and Fe doped hydroxyapatite: novel biomimetic UV-filter for sunscreen formulation

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The use of sunscreens as protective barriers against skin damage and cancer, by absorbing harmful UVA and UVB rays, is becoming an increasingly important issue; such products are usually containing titanium dioxide (TiO₂) or zinc oxide (ZnO). TiO₂ is able to reflect, scatter and absorb UV radiations, thus preventing sunlight-related skin disorders such as sunburn and skin photodamage. However, TiO₂ is well known to generate reactive oxygen species (ROS) under photoexcitation, it has to be chemically modified when used in sunscreens. Calcium phosphate (CaPs), especially hydroxyapatite (HA) have been deeply investigated for several applications in biomedical field and nanomedicine due to their high biomimicry and biocompatibility. An interesting feature of biomimetic HA is to incorporate some foreign ions in its lattice, in fact, in the past years we developed a number of protocols for the introduction of different kind of ions (e.g. Mg, Sr, CO₃, Fe (II, III)) and the achievement of multifunctional products for regenerative- and nano-medicine. However, regarding sunscreens, HA does not absorb in the UV range, so we decided to modify its structure to obtain a UV-absorbing material. Doping with appropriate elements may provide final compound with promising UV protection. In this study two different hybrid materials were successfully developed exploiting the biomineralization process; one is composed of gelatin and Ti-doped HA (gel-TiHA) and another of gelatin and Ti-Fe(III)-doped HA (gel-TiFeHA). During the biomineralization process the mineral phase is nucleated on gelatin molecules blocking the particles' growth and allowing the formation of nanocrystals merged in the polymer matrix. This hybrid composition allows an easy dispersion in sunscreen formulations without damaging skin for penetration of nanoparticles. Deep investigations were performed to evaluate the particles' morphology (SEM), chemical properties (XRD, FT-IR, TGA) and interaction with UV-VIS radiations (adsorption spectra and photodegradation potential). Results demonstrate that the sample with gel-TiHA revealed a high reflectance in the UVA and UVB range however, the sample with gel-TiFeHA showed a good absorption only in UVB. Although the worst properties of gel-TiFeHA it is important because the presence of iron ions provide for a brown color to the particles, thus avoiding the whitening effect typical of highly protective sunscreens. Furthermore, both samples do not show photocatalytic effect thus avoiding the formation of radicals and/or reactive species under irradiation and highlighting their potentiality for innovation in sunscreens. In conclusion, we developed hybrid particles capable to protect by UVA and UVB rays, avoiding the whitening effect and the photocatalytic effect which can damage the tissues provoking skin disease.

#087 - Amyloid fragments and their toxicity on neural cell

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Background: The formation of nanoscale amyloid fibrils from normally soluble peptides and proteins is a common form of self-assembly phenomenon that has fundamental connections with biological functions and human diseases. Recent findings implicate that fibrillation products, the protein aggregates formed during the various steps leading to formation of mature fibrils, induce neurotoxicity predominantly in their intermediate oligomeric state.

Results: Lysozyme, as model protein in our study, was converted from its soluble native state into highly organized amyloid fibrils under agitation during heating in acidic pH conditions. Ultrasonic treatment (UST) was used to break amyloid-like fibrils and create well-defined structures-seeds. Atomic force microscopy (AFM) and fluorescence microscopy was employed to characterize the morphology of the various amyloid assemblies obtained (from proteins, prefibrillar intermediated, fragmented fibrils to mature fibrils) and neural cells-amyloid complexes. Our results demonstrate that aggregates exhibit toxicity, although native proteins and fibrils appear to have no effect on number of cells. We revealed that prefibrillar intermediated and their mixture with proteins lead to a decrease in the number of cells.

Conclusions: Protein aggregates, even those irrelevant to disease, can promote toxic actions in neuronal cells. Our findings confirm that innocuous hen lysozyme can be engineered to produce both cytotoxic soluble prefibrillar aggregates and non toxic mature amyloid fibrils. Our work further strengthens the claim that fibrillar conformation, and not the identity of the protein, is key to cellular toxicity and the underlying specific cell death mechanism.

#088 - Additive manufacturing of thin structures in NiTi shape memory alloy by laser metal wire deposition and laser powder bed fusion: martensitic transformation and microstructures

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Additive manufacturing (AM) of NiTi shape memory alloys has been a challenging topic for developing advanced smart elements for sensors and actuator as well as biomedical devices, such as stents. The laser melting of different feed stocks, such as powder and wire, has an important role on inducing tailored microstructure and functional performances, due to different cooling rates.

In this work Nitinol characteristics induced by using two laser based AM techniques, namely laser metal wire deposition and selective laser melting, were investigated. The evolution of the martensitic transformation was studied from the initial feed stock, wire and powder, to the AMed samples, in as built and heat treated condition, via differential scanning calorimetry and X-Rays diffraction in

temperature. The microstructure and chemical composition were investigated through optical and scanning electron microscopy coupled with energy dispersive spectroscopy.

Aspect ratio and size of the solidified liquid pools are strongly associated to the different AM techniques and feed stock materials, while the rule of post- heat treatments is fundamental for fixing the functional properties of the NiTi built parts.

#089 - Capillary assembly of hybrid colloidal clusters - From plasmonic structures to microswimmers*Heiko Wolf (1) - IBM Research - Zurich**Other Authors: Songbo Ni (1,2), Miguel Angel Fernandez Rodriguez (1,2), Jessica Leemann (1,2), Emanuele Marini (1,2), Ivo Buttinoni (2), Laura Alvarez-Frances (2), Lucio Isa (2), Heiko Wolf (1) (1) IBM Research – Zurich, Säumerstrasse 4, 8803 Rüschlikon, Switzerland. (2) Laboratory for Interfaces, Soft Matter and Assembly, Department of Materials, ETH Zurich, Vladimir-Prelog-Weg 5, 8093 Zurich, Switzerland.*

Patchy colloids have drawn a tremendous attention over the past years owing to their great potential in constructing colloidal superstructures as well as in fabricating active colloids. Despite the remarkable progress in fabrication of patchy particles, current methods are commonly limited to simple compositions and geometries. Here, we present a method based on sequential capillary assembly on topographical templates (sCAPA), which achieves unprecedented control over composition and geometry.

We applied sCAPA for the programmable assembly of hybrid nanoclusters as well as for the fabrication of colloidal microswimmers. Metallic hybrid nanoclusters are interesting plasmonic materials with tunable resonances and strong field enhancement at interparticle junctions. Colloidal microswimmers are currently explored as models for out-of-equilibrium systems, with the promise of being used as micro- and nanoscale devices for health and environmental applications. They convert uniform sources of fuel or uniform external driving fields (e.g. magnetic or electric) into directed motion by virtue of asymmetry in their shape or composition. We use sCAPA to link microspheres of different materials into hybrid colloidal clusters of designed shapes that can actively translate, circulate, and rotate powered by asymmetric electro-hydrodynamic flows.

#090 - NANOPARTICLE-SURFACTANT COMPLEXES AT THE OIL / WATER INTERFACE*Davide Orsi - University of Parma**Other Authors: Davide Orsi (1), Libero Liggieri (2), Sara Llamas (2), Francesca Ravera (2), Eva Santini (2), Mario Campana (3), Luigi Cristofolini (1,2) 1) Dept. of Mathematical, Physical and Computer Sciences, University of Parma, Italy 2) CNR – Inst. for Condensed Matter Chemistry and Energy Technologies, Genoa, Italy. 3) STFC Rutherford Appleton Labs - Harwell Oxford, Didcot, United Kingdom*

Pickering emulsions, i.e. emulsions stabilized by solid particles, are important in many food, cosmetic and pharmaceutical applications. Even if they have been known for more than a century, they still pose important challenges to the researchers.

We report on a neutron reflectivity (NR) study of the layers formed by amphiphilic complexes of silica nanoparticles (NP) and cationic surfactant CTAB at the oil (dodecane)-water interface. Dilational rheology and interfacial tensiometry provided a general understanding of NP-surfactant layers at liquid interfaces [1], but have also evidenced a complex interplay between the components. In particular, it is still unclear if reorganizations of surfactant-NP complexes and/or a redistribution of the surfactant between the complexes and the free liquid interface may occur at the interface[1,2].

To elucidate these aspects, we employed for the first time NR [3] to study these complexes at the interface. Experiments were performed on INTER (ISIS, Rutherford Appleton Labs) on a set of different contrast matched sample. We investigated the mixed layer structure and the redistribution of surfactant between the different interfaces: particle/oil, particle/water, water/oil. Accurate modelling of the data allows to estimate the contact angle, an important parameter in determining the stability of Pickering emulsions. We find evidence of an oil/water emulsion layer at the interface. Results are discussed in the light of previous findings.

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#091 - Understanding the bio-interface at the nanoscopic level: the case of Cys/Ag(110).*Letizia Savio - CNR-IMEM**Other Authors: Marco Smerieri (CNR-IMEM), Giovanni Carraro (DIFI-UNIGE), Luca Vattuone (DIFI-UNIGE), Mario Rocca (DIFI-UNIGE), Igo Pis (Sincrotrone ELETTRA), Silvia Nappini (CNR-IOM), Elena Magnano (CNR-IOM)*

Adsorption and self-assembly of (bio)-organic molecules at surfaces is a key issue in nanoscience and nanotechnology for the many possible uses of the hybrid organic-inorganic interfaces. Depending on the nature of the molecules, applications are foreseen in the fields of molecular electronics, sensoristics, pharmacology, bio-compatibility, hygiene and bio-fouling.

In this frame, amino acids (AA) have a key role since they are the basic constituents of peptides and proteins and are simple enough to bring information on the chemical interaction of some biological functions with the surface. They are therefore among the most used molecules in fundamental studies aiming at the characterization of the hybrid organic-inorganic interface at the molecular level [1].

In my talk, I will discuss our recent results on cysteine adsorption at Ag(110), which is investigated by combining low temperature scanning tunnelling microscopy and high resolution XPS and NEXAFS investigations. As it is the case for several AA [1,2], cysteine layers organize on Ag(110) in different phases depending on surface temperature, suggesting the existence of several local minima in the energy diagram of these systems. The chemical nature of the Cys molecules is correlated to the self-assembled geometry of the layer and simple adsorption models are proposed [3] based on the experimental data and on the comparison with other systems [1].

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#092 - Fingerprints of sp¹-carbon hybridization in the core-level spectra of surface-grown materials

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The advent of on-surface chemistry and molecular self-assembly opened the way to the realization of organic materials whose lack of stability in vacuo would otherwise forbid their synthesis. A famous example is the formation of graphene nanoribbons with tunable width by polymerization of properly designed molecular precursors. Recently the on-surface coupling of the precursors have also been used to synthesize adsorbed organic systems with chemically vulnerable linear carbon chains with sp¹ hybridization. [1] Another advantage of on-surface synthesis is that the full realm of the experimental and theoretical surface science toolbox is available for the investigation.

While the method of choice for surface-supported architectures is the scanning tunneling microscope and ultimate resolution is achieved by low-T non-contact atomic force microscopy, electron core-level spectroscopy can provide an even more local and sometimes insightful probe of the electronic properties of the material, as we show here.

We present ab initio investigations of the core-level spectral properties of a paradigmatic mixed sp¹/sp² C polymer, recently synthesized on Au(111) in linear/2D forms, and constituted by alternated biphenyl and linear C₄ units, to discuss the appearance of the sp¹ hybridization typical of linear C chains in the spectra. X-ray photoemission (XPS) and polarized near-edge X-ray absorption fine structure (NEXAFS) spectra are evaluated for the polymer in vacuo and on the metal surface, in the framework of density functional theory simulations with core-excited C potentials that have successfully reproduced spectral dichroisms [2]. We find that, at variance with the XPS spectra that do not easily show the signature of sp¹ hybridization, NEXAFS spectra can distinctly fingerprint the sp¹ part of the polymer through polarized spectra. Such capability is further facilitated by the different degree of hybridization of the molecular orbitals at the interface for the sp¹ and sp² states.

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#093 - High thermal stability in graphene-based molecular spin interfaces

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Paramagnetic metal organic molecules can open the route to engineer spintronic devices when their magnetic moments are stabilized against thermal fluctuations, e.g. by a controlled interaction with a magnetic substrate. We report on robust spin interfaces, exhibiting a residual magnetic coupling up to room temperature (RT), with tunable (anti- or ferromagnetic) alignment constituted by Metal Phthalocyanine (MPc) ordered arrays on a Co-intercalated Gr substrate. The (anti)ferromagnetic response of the spin interface is determined by a symmetry-selected superexchange path, actively mediated by the Gr sheet and the organic backbone of the MPc molecules (see Ref.1 for details).

The fundamental role of the occupation and symmetry of the magnetically active molecular orbitals suggests that the magnetic response of such interfaces can be further manipulated, e.g. by doping, thus opening to a route for the fabrication of metal-organic spin interfaces, robust against thermal fluctuations, with fully-controlled properties.

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#094 - Characterization of the CoPc/Bi₂Se₃ interface

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Topological insulators are a promising class of materials for innovative applications in the field of spintronics, for example, where they can be exploited to implement spin generator, transport, or torque devices. New perspectives in this field can arise from the interface with transition metal (TM) tetrapyrroles complexes, porphyrins or phthalocyanines, which can perturb, either enhancing or suppressing, spintronics relevant properties, such as spin coherence. In a recent study [1] an interplay between the topological state and the molecular adsorbate was found and the system has shown potential to lead towards a whole new class of spintronic devices. In this context we characterized the interface of Bi₂Se₃ and a metal phthalocyanine, namely the cobalt Pc (CoPc), from sub-monolayer to thin film, by means of Inverse Photoemission and Photoemission Spectroscopy. These measurements provide complementary information to a time resolved photoemission experiment, performed at the Laboratory of Quantum Optics, to investigate the charge transfer phenomenon between the molecule and the substrate.

Combined UPS-IPS measurements enlighten the occupied-unoccupied electronic Density of States. The energy alignment of the unoccupied molecular states with the unoccupied states of the Bi₂Se₃ substrate could provide a channel for the photoinduced charge transfer between the substrate and the molecule, particularly interesting for the implementation of these interfaces in real life devices. We are also particularly interested in the appearance interface states that should be the key to the interactions occurring between the substrate and the molecules. In our measurements, we found that the submonolayer-single layer CoPc deposition leads to the intensity increasing and broadening of the surface Bi₂Se₃ feature at about 0.3 eV above the Fermi level, together with the appearance of a molecular orbital at about 1 eV confirming the hybridization of the molecular states with the substrate. Photoemission data confirm the finding of reference 1, where, at low coverages a blurring of Bi₂Se₃ bulk states is observed strongly indicating the hybridization with molecular orbitals. At higher coverages features that can be attributed to Bi₂Se₃/CoPc interface states were observed. Preliminary time-resolved photoemission measurements in the femtosecond time scale, on CoPc thin film on Bi₂Se₃ confirm the literature charge transfer mechanism, with no evidence of substrate ordering effects.

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#095 - Role of surface oxidation in the interaction and self-metalation of 5,10,15-triphenylcorrole with Cu(111)

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Tetrapyrrolic macrocycles belong to one of the most widely used scaffolds for the construction of self assembled supramolecular architectures on surfaces. In this framework, metallo-porphyrins are a very important class of molecules for their possible use in novel devices based on the interaction of an active nanoscale site with the surrounding medium. Moreover, they can be taken as templates for the ordered organization of “isolated” metallic atoms, which correspond the metallic ions at the center of the macrocycles. The fine control on the self-assembling and, possibly, on the metalation of the molecules represent a key issues in the development of these organic-substrate interfaces with the aim of tailoring suitable properties for organic-based devices. In the last decade many groups studied the in-vacuo metalation of porphyrins [1] in order to understand how they (metalated or not) interact with the substrates and in which way the self-assembled organic monolayer can be controlled and modified. In the case of self metalation, a porphyrin molecule is deposited on a metal surface and the metalation happens by picking up a metal atom from the substrate, already at room temperature (RT) or, in other cases, by a thermally treatment. Recently, on oxygen adsorbed Cu(100) and Cu(111) surfaces, it has been observed that the self-metalation occurs at a lower temperature than on the same clean surfaces [2,3] with the formation of H₂O. Among the family of tetrapyrrolic-based molecules, no study was performed on the 5,10,15-triphenylcorrole regarding the possibility to evaporate it in vacuo and its growth and stability on surfaces, self-assembly, electronic properties and metalation. Therefore we deposited 5,10,15-triphenylcorrole on the clean and the oxidized Cu(111) and fully characterized it by means of X-ray Photoemission (XPS) and Near Edge X-ray Absorption Spectroscopy (NEXAFS) at the ALOISA

beamline (Elettra, Trieste). Fast XPS spectra of the N 1s core level have been recorded during annealing in order to find the temperature at which the metalation sets up. On the oxidized surface the metalation temperature is lowered of about 90 K with respect to the clean surface, confirming the role of oxygen. Moreover, it was possible to monitor the relative peak height of the N 1s XPS spectrum of the corrole: on the clean surface we observe a 1:1 peak ratio between the pyrrolic and the iminic components, instead of the stoichiometric 3:1, evidencing a surface-induced loss of one of the 3 H atoms of the pyrrolic group, as previously observed on the Ag(111) surface [4].

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#096 - Inverse photoemission investigation of unoccupied density of states for Phthalocyanines on gold (110) and (111) substrates

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In order to exploit the potential of metal phthalocyanines (MPc) for novel electronic devices, it is crucial to gain understanding of occupied as well as unoccupied energy level alignment at metal-organic interfaces [1]. Inverse photoemission spectroscopy (IPES) can be efficiently utilized to unravel unoccupied energy level alignment at the interfaces, thereby providing useful information about interfacial electronic properties at metal-organic interfaces. The interest of such studies is due to the observation that empty orbitals are more sensitive to the intermolecular interaction due to their higher delocalization around the macrocycle. The objective of the study is to employ IPES to enlighten the differences, present in the literature [2] of MPc layers induced by symmetries and bond differences onto iso-elemental substrates, providing a coherent picture of interface electronic structure of CoPc and CuPc induced by the different occupancy of 3d level of the central metal atom. We have monitored the evolution of IPES spectra with increasing thickness of CoPc and CuPc thin films on the high anisotropic Au(110)-(1x2) and compared with the same layers grown onto the close-packed Au(111) substrate. Empty molecular states grow with the film thickness and become prominent at 0.7 ML in all cases. In case of CuPc deposition a weak interaction takes place. The molecular features are clearly defined at the submonolayer coverages, remaining substantially unchanged with thickness increasing and the lowest unoccupied molecular orbital (LUMO) is found slightly shifted toward the Fermi level, i.e. at lower energies, with respect to the LUMO energy in the multilayer coverage, for both substrates. In case of CoPc deposition a stronger interaction localized at the central Co atom in the molecule with gold takes place in both substrates. Differences in the empty orbital energies are found in the two cases as a function of submonolayer coverages, that suggest a specific redistribution of the molecular orbitals as a function of the structural phases. Moreover, onto Au(110), a clear interface state has been observed near the Fermi level for the deposition of CoPc at submonolayer coverage. Theoretical calculations show that Co 3d orbitals with z component delocalize around the Fermi level due to interaction with the substrate. The dissimilarities in the interfacial interaction observed by IPES measurements for the deposition of CoPc and CuPc on Au(110) are also supported by direct photoemission data.

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#097 - Graphene-based negative electrodes for innovative Na-ion batteries

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Nowadays, rechargeable Li-ion batteries (LIBs) represent the state-of-the-art for the power supply in technological devices [1]; however, the large-scale implementation of this technology, for example in the automotive field, would raise issues, especially concerning the limited lithium mineral reserves. The investigation of alternatives to lithium is hence strongly desirable, although it requires the identification of new materials suitable as components for new batteries, possibly displaying even better performances for the current commercial systems. In this framework, graphene-based materials appear as rather good candidates for this purpose. In fact, it is known that chemically produced graphene is suitable for development of high-capacity LIBs, in virtue of its electronic, mechanical properties and porosity.

Recently we found that anodes based on graphene derivatives can also support the insertion of Na⁺ ions with high capacity and stability upon cycling [2]. In particular, thermally exfoliated graphene oxide (TEGO) produces capacities of 248 mAh/g after 50 cycles, H-treated TEGO shows reversible capacity of 491 mAh/g after 20 cycles, while Ni-nanoparticles decorated TEGO displays up to 420 mAh/g reversible capacity after 25 cycles with 97% coulombic efficiency. Solid state ²³Na NMR performed on different chemically synthesized graphene materials allowed us to shed light on the mechanism of sodium insertion/extraction on the defective graphene surfaces [3]. These findings indicate the feasibility of the development of novel Na-ion batteries (SIBs), whose research is still at an early stage, just because of the lacking of suitable Na anode materials [4].

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#098 - Three-dimensional microporous graphene decorated with lithium

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Carbon atoms arranged in a honeycomb lattice belong to a much larger family of 2D systems including materials with very different properties in terms of morphology, lateral dimensions, number of layers and defects, that are ready to be integrated in a plethora of technological applications. Graphene maximizes the surface area per weight but, for many applications [1-2] it is useful to pack the individual layers of graphene into a compact and interconnected 3D arrangement to maximize the amount of surface-area available in a given volume. This motivates a strong research effort towards the design of porous graphene architectures aimed at controlling the topological structure and pore size of continuous networks of graphene sheets to optimize the desired functionalities [3-5].

We present here a spectro-microscopy study of stable micro-porous 3D graphene structures produced by Chemical Vapour Deposition following a procedure similar to that described previously [6] but suitably modified to obtain a thinner graphene coverage.

The 3D graphene structures present the properties of few-layer graphene with a low density of defects and of unsaturated dangling bonds at the edges, as evidenced by Raman and core-level photoelectron spectroscopy. Micro-porosity demonstrates a high capability of storing Li into the interconnected network, with approximately 50% higher capacity than graphite. The morphology also allows Li atoms to be hosted in a 1/4 Li:C ratio, higher than graphite but less than graphene micro-flakes. In the latter case, the high defect density at the edges strongly binds Li to the edges enhancing the Li/C content, while the low defect density of MPG, despite a lower Li/C content, can induce a low Li-C binding energy, thus suggesting an improved cyclability for applications of MPG requiring Li accumulation. These large micro-porous suspended graphene networks constitute a good compromise to maximize the content of cyclable Li per volume unit onto a stable few-layer graphene continuous architectures, while avoiding the detrimental effects of trapping defect sites and of small size of the typical graphene flakes.

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#099 - Graphene-enhanced loop heat pipes for space applications

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Loop heat pipes (LHP) are used for the passive removal of heat from a source by capillary action [1]. Since they do not need any mechanical parts, they require less maintenance than traditional pump-based thermal control systems [2]. Hence there are used as cooling systems for electronic components in space vehicles and satellites [3]. A key part of an LHP is the porous medium, known as a wick [1]. This is generally made of Ni [4] or stainless steel (SS) [5], and has the dual role of driving the capillary action and transferring heat to the liquid. Any improvements in capillary pressure and/or thermal conductivity in the wick can promote the operation of the overall system [1][6][7]. Here we report the use of graphene to coat metallic wicks in LHP, by following two approaches. In one, Chemical Vapour Deposition (CVD) is used to grow multilayer graphene on SS wicks, followed by a thermal treatment in air to make it more hydrophilic so that it interacts better with the working fluid. In the second, a water solution of reduced graphene oxide and carbon nanotubes is infiltrated into the wick and freeze-dried to produce a hierarchical foam structure. Both approaches result in a capillary pressure increase of up to 50%. The performance of these wicks is studied both on ground and under microgravity conditions, and preliminary analysis shows an improvement in the evaporation rate of up to 8 times compared to the uncoated reference wick. These results are very promising for the future application of graphene-based LHP in space vehicles and satellites, as well as energy plants, data centres and train thermal management systems.

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#100 - Effects of water on MoS₂ and graphene lubricity: a quantum mechanics/molecular mechanics approach to tribochemistry

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Graphite and molybdenum disulphide (MoS₂) are well known solid lubricants. The possibility to peel off single layers from their bulk structures renders these materials very promising for nanoscale applications, where the thickness of the lubricant should be reduced to the atomic level. It is well documented that the lubricity of MoS₂ is adversely affected by air humidity, while graphite depends on moisture for good lubricating properties. The microscopic origin of such behaviors is still unclear, thus atomistic simulations represent a very powerful tool to shed light into these processes.

We carry out ab initio molecular dynamics simulations also adopting a quantum Mechanics/Molecular Mechanics (QM/MM) approach to study the interaction between water molecules and graphene/MoS₂ multilayers and ribbons. Shear and Load stresses are applied during the simulations, mimicking tribological conditions. The rate of tribochemical reactions observed in graphene is much higher than that observed in MoS₂ [1,2], as expected from the higher energy of graphene edges than MoS₂ ones.[3,4] Our results suggest that the saturation of graphene edges by dissociated water molecules is the key process for providing interlayer slipperiness. On the contrary, in MoS₂ chemical reactivity seems to be less important at ordinary temperatures even in the presence of defects. Moreover, by monitoring the layer velocity for different water coverages, we identify a negative effect of intercalated water molecules on interlayer slipperiness. These outcomes suggest that water molecules physically interacting with MoS₂ layers impede sliding even in the absence of any chemical oxidation [4].

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#101 - Tribocatalytic conversion of Methane to Graphene on Sliding Nickel Surfaces

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Graphene and other carbon-based nanostructures are known to provide remarkable friction and wear performance but without continuous replenishment, they wear out, and thus high friction and wear prevail again. We show dissociative extraction of graphene and disordered carbon from methane molecules on the sliding surfaces of Ni. In a steel on steel sliding experiment it is observed, by means of Raman spectroscopy and tunnel electron microscopy, that methane is converted to a tribofilm consisting of graphene and other carbon nanostructures if steel is coated by a Ni-VN nanocomposite. The carbon based tribofilm is shown to reduce the friction coefficient by nearly 50% [1].

By means of ab-initio Molecular Dynamics simulations we identified the initial stage of tribologically induced formation of 2D carbon nanostructures from CH₄ molecules. The process is initiated by CH₄ dehydrogenation, which is highly accelerated by the tribological conditions: the process is endothermic at the open surface in static conditions, while it occurs almost instantaneously at the tribological interface. The detached H atoms diffuse into the Ni bulk, and the interfacial C atoms become interconnected within chains that form an amorphous film of low density. The load and shear stresses applied to the carbon film sandwiched between the Ni surfaces promoted the rehybridization of C atoms and the formation of sp² planar structures with the same lattice parameter of Ni(111). The newly formed hexagonal rings constitute the first nucleation centers for graphene growth. Eventually the amorphous film self-organizes into two separate graphene flakes adsorbed on the sliding surfaces.

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#102 - Graphene devices for IoT, automotive and aerospace applications: two case studies

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A key target for modern technology is to replace metals with lighter, cheaper, less energy-consuming materials. This “metal replacement” goal is already well established for structural applications in aeronautics and automotive, where the search for higher efficiency and reduced CO₂ emission is pushing toward the use of carbon-based materials (e.g. carbon fiber composites and high-performance polymers), replacing up to 50% of the metal parts of the vehicle¹.

In this talk, we describe how graphene can replace with success metals in two case studies recently developed in our group: the fabrication and characterization of graphene Near-Field Communication devices² and graphene based heaters for aeronautical and automotive applications.

The high conductivity and high flexibility of graphene-based conductive paths make the processing easy on a wide variety of substrates materials with no need of high temperature processes and can be applied both on flat or curved objects. Being composed of carbon, the conductive paths will be highly chemically and thermally stable, resistant to acids, oxidation, high temperature and saline environments. Moreover, the processes used for the realization of these applications are scalable, environmentally friendly and make use of a technology already present in the industries.

The good performance of the graphene NFC devices prepared open a new scenario in the field of flexible electronics and communication technology, paving the way for the realization of wearable electronic devices embedded in fabric for new IoT applications.

The graphene heaters realized show a good functionality both integrated in carbon fiber reinforced composites both on flexible substrates, with an improvement in stability and sustainability. These qualities look promising for future applications in aerospace and automotive like anti/de-icing modules.

Graphene and related materials are expected to revolutionize many application fields as their outstanding properties suggest that they can replace other materials in existing applications.

¹ Airbus: <http://www.airbus.com/newsevents/news-events-single/detail/composites-help-keep-next-generation-airbus-aircraft-eco-efficient/>.

²“Application of graphene-based flexible antennas in consumer electronic devices”, A. Scidà et al., Materials Today 21, 223, 2018

#103 - Graphene-based scaffold for energy storage

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Graphene-based nanomaterials attracted considerable interest in the development of new nanostructured scaffolds to be used as efficient solid-state storage devices. Understanding, at the atomic level, the mechanism of interaction between chemical species (molecules, metal clusters, ions, ionic liquids, etc.) and the irregular network of these nanostructured materials is crucial to improve the properties of this new class of devices. Here, we proposed and implemented an algorithm to generate graphene scaffolds with a given porosity and specific density and a realistic structure. A number of different structures have been generated and characterized with respect to their hydrogen adsorption capacity. Furthermore, we modeled a set of graphene based supercapacitors to rationalize the capacitive mechanisms and to increase the energy storage performance of these devices.

#104 - Investigation of Amorphous Silicon-Based Sub-Stoichiometric Oxide and Oxynitride Thin Films for Photovoltaic Applications with Multi-Characterization Approach

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Since 1970, crystalline silicon technology controls almost the 90% of the whole photovoltaic market, since silicon is abundant, non-toxic and stable material, with well-known physical properties [1]. Silicon heterojunction (SHJ) solar cells have now achieved a record efficiency of 26.7% due to high-quality ingot growth processes and solar cell technology [2]. As crystalline silicon wafers have reached such a high purity, further device advances now rely on innovation in surface passivation schemes.

To improve the interface passivation between the c-Si substrate and the doped film of the heteroemitter in SHJ solar cells, a few nm thick buffer layer of intrinsic a-Si:H is usually inserted. However, a-Si:H films present high parasitic absorption of light, causing loss in short circuit current, and high series resistance. Strategies to minimize absorption are based on widening the optical band gap through the incorporation of carbon, nitrogen or oxygen in the amorphous matrix [3,4] leading to the formation of sub-stoichiometric Si oxides and oxynitrides. Despite the importance of these complex materials in different fields [5,6], the influence of N and O inclusion on carriers' recombination processes at surfaces and interfaces is still not clear.

The present contribution aims to characterize sub-stoichiometric a-SiO_x and a-SiO_xN_y thin films' structure and surface passivation properties. The layers have been deposited by plasma enhanced chemical vapour deposition with increasing fractions of N₂O or CO₂ gas added to the SiH₄ plasma. Several techniques, namely Fourier-transform infrared spectroscopy, spectral ellipsometry, surface photovoltage spectroscopy and photo conductance decay have been employed to analyse structural and optical properties, light-induced electronic transitions and minority carrier lifetimes.

With the combination of all methods, the influence of N₂O or CO₂ fluxes on interface properties has been clarified. On the one hand, adding a higher flux ratio causes increasing disorder in the amorphous network and microvoid formation, with consequent reduction of passivation quality. On the other hand, the optical band gap becomes larger than the one of pure a-Si:H layers, reducing parasitic absorption. In summary, the introduction of N₂O and CO₂ during deposition of a-Si:H is both beneficial and detrimental at the same time and a moderate inclusion can lead to the suitable layers for SHJ solar cells application. The use of a multi-characterization approach has led to optimization of the deposition conditions of the layers.

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#105 - Correlation between spectroscopic, electric and optical response in Al:ZnO films

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Transparent Conducting Oxides have gained large interest because of the peculiar combination of high transparency and low electric resistivity, with applications in optoelectronics and plasmonics.[1] Their properties can be largely tuned by means of suitable dopants in wide-band gap semiconductors matrix over a large range of concentration (like in Al-doped ZnO). However, the presence of structural defects results in an unpredictable complexity that prevents a clear identification of chemical and structural properties of the films, thus their identification and control is highly desirable.

We have exploited the chemical sensitivity of Hard X-ray Photoelectron Spectra and Near Edge X-ray Absorption Fine Structure in combination with DFT to determine the spectroscopic response of defects in Al:ZnO films. Modifications in O1s and O K-edge have allowed to determine the concentration of embedded H, Zn vacancies and O interstitials in undoped ZnO. Contributions coming from substitutional and interstitial Al atoms have been identified and related to changes in the oxide stoichiometry and an increased oxygen coordination, together with small lattice distortions.[2] Consequences on the optical response in the UV-VIS-IR, band populations and

on electric response are discussed, taking into consideration also the thickness reduction. This provides a tool to control the material response and improve the performance of TCO films.

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#106 - Supercapacitive properties of Ni-based nanostructures grown by chemical bath deposition

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In recent years Ni-based nanostructures have attracted great attention for electrochemical energy storage applications. One of the most promising nanostructure explored so far is represented by the Ni(OH)₂ nanowalls, a tight network of interconnected nanosheets grown by low-cost chemical bath deposition (CBD) [1]. Despite the impressive supercapacitive performances, the specific capacitance of the nanowalls is still below the theoretical value. In this work, we present a novel Ni nanostructure, called Ni/Ni(OH)₂ core-shell nanofoam, with a very high surface over volume ratio and superior features in terms of specific capacitance and stability. Scanning electron microscopy (SEM) reveals that after a reducing annealing the Ni(OH)₂ nanowalls is transformed into an ensemble of interconnected Ni nanoparticles (20-30 nm in size), called Ni nanofoam. Cyclic voltammetry (CV) in alkaline solution is used to electrochemically oxidize the surface of the Ni nanofoam, producing an outer shell of Ni(OH)₂ active species, as confirmed by transmission electron microscopy (TEM). The supercapacitive behaviour of the Ni(OH)₂ nanowalls and Ni/Ni(OH)₂ core-shell nanofoam is investigated by CV, galvanostatic charge-discharge tests, and electrochemical impedance spectroscopy (EIS) in 1 M KOH. Superior specific capacitances are achieved by the Ni/Ni(OH)₂ core-shell nanofoam for all the investigated current densities. The enhanced supercapacitive properties are related to the metallic core of the core-shell architecture, which improves the overall charge transport. This work offers a new strategy to enhance the energy storage performances of conventional Ni(OH)₂-based nanostructured electrodes.

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#107 - Lithium adsorption on graphene at finite temperature

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The increasing demand for high energy density lithium ion batteries motivates a search for alternative electrode materials. Experimentally obtained graphene based structures have been suggested to replace the state-of-the-art graphitic anode. For a thorough characterization of Li adsorption on graphene, we study the interaction of Li with graphene both at zero and finite temperatures.

The zero temperature study was carried out by means of density functional theory (DFT) accounting for van der Waals interactions while the finite temperature behavior was studied by Monte Carlo techniques with DFT-derived Li-graphene interaction potential constructed via cluster expansion method. The zero temperature calculations show that Li-graphene interaction is mainly electrostatic and dispersed Li ions are unstable with respect to bulk Li. At higher temperatures, entropic effects stabilize lower concentrations with respect to bulk Li. At temperatures below 400 K, we found that at any given chemical potential, the formation of 2D Li-clusters is stable over a random distribution of Li on graphene. Our calculations reveal different ordering of Li-clusters such as Li-islands and Li-strips. The formation of the Li-strips is however due to the finite size of the simulation cell and therefore, the Li-islands phase is expected to dominate in the thermodynamic limit.

#108 - Ordering in the cation sub-lattice in AgxBi1-xS2 nanoparticles for photovoltaics by XAFS

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Nontoxic environmental friendly AgBiS₂ nanoparticles (NPs) in the form of thin films (40 nm thickness) exhibit 6.4 % certified photovoltaic efficiencies [1]. The high efficiency is associated to its high optical extinction (>10⁵ cm⁻¹) combined to a nearly 100 % internal quantum efficiency across the VIS and NIR part of the optical spectrum. However, the photovoltaic performance is limited by the presence of electronic midgap trap states which limit the maximum allowable thickness of films within a solar cell. The structural origin of these traps remains unknown; in fact, the atomic structure itself of AgBiS₂ NPs is yet to be thoroughly understood.

A key issue in this context is how Ag and Bi are distributed within the cation sub-lattice; this degree of ordering is a structural variable, limiting cases of which are chemical order, clustering and a random distribution. In fact, it is known that different types of ordering are found in minerals with AgBiS₂ composition. Matildite is the most common AgBiS₂ mineral, having hexagonal structure. A polymorph of Matildite is Schapbachite having rock salt cubic structure stable at high temperatures. The unit cell of Matildite can be derived from

Schapbachite's as long as some order exists on how Ag and Bi are distributed on the cation sub-lattice. At high temperatures (> 287 °C) disorder takes place and cations are distributed randomly. The disordered Schapbachite structure can be stabilized by alloying with Pb [(AgBi)_{1-x}Pb_xS₂ with x up to 0.4] [2,3].

X-ray absorption fine structure (XAFS) is the premier experimental probe of ordering in alloys. Consequently, in order to shed light on the local structure of AgBiS₂ NPs we have performed XAFS measurements on the LISA beamline of the ESRF. Three sets of samples (different Ag/Bi ratio, different growth temperature and Pb added samples with different percentage) were measured at the high energy Ag K-edge. The XAFS spectra can be analysed based on a modification of monoclinic Ag₂S in which Bi partially substitutes Ag in the second shell. By comparing the second shell composition to the average composition we show that the distribution of Ag and Bi is random. In Pb containing samples we show that at 10% concentration Pb substitutes only Ag while at 20% it substitutes both Ag and Bi. These results will be discussed in relation to the samples' physical properties.

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#109 - Novel Geopolymer-based oxygen carriers with potentials for chemical looping processes

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Chemical Looping Combustion with or without oxygen uncoupling (CLC and CLOU, respectively), are promising technology developed to achieve inherent CO₂ separation during combustion with high efficiency and low costs. Both CLC and CLOU processes involve the use of a metal oxide which acts as a carrier of the oxygen needed for the combustion, with possible release of gaseous O₂ at high temperature, therefore allowing also for the conversion of less reactive solid fuels. However, one of the main drawbacks of these processes mainly derives from the scarce stability at high temperatures and under continuous cycling of the inert support material, with which the metal oxides are usually coupled, and the environmental and economic impact of the current oxygen carriers (OCs) production technologies. In this work, geopolymers are investigated as innovative, low cost and sustainable support matrices for OCs loaded with various metal oxides, for CLC and CLOU applications. Different formulations based on Cu, Mn and Fe oxides have been obtained, and their performances in terms of red-ox activity, oxygen transport ability and oxygen uncoupling have been evaluated through cycling tests in thermobalance and in a lab-scale reactor, under representative conditions between 700 and 900 °C. Attrition tests were also conducted to evaluate the abrasion resistance of the materials and their suitability for the use in fluidized bed conditions. First results are promising, showing good oxygen transport ability and a good stability upon repeated cycles at high temperatures. Mn and Cu-based OCs were also able to release oxygen in inert atmosphere, thereby demonstrating potentialities for CLOU applications.

#110 - MOLECULARLY IMPRINTED POLYMERS FOR SELECTIVE REMOVAL OF EMERGING CONTAMINANTS FROM WATER

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In the recent years there has been an increasing interest on the environmental risks related to the so called “emerging contaminants” (ECs) in wastewaters, as the traditional methods are not able to efficiently remove them. The ECs originate from a variety of product types including human pharmaceuticals, veterinary medicines and personal care products. The most common ones are the highly prescribed non-steroidal anti-inflammatory drugs, such as diclofenac.

We propose molecularly imprinted polymers (MIPs) as valid tools for selectively removing of these drugs from water. MIPs are synthesized by polymerization of cross-linking and functional monomers in the presence of a target analyte, which acts as a molecular template. Following the polymerization, the template is removed to leave cavities with selectivity for the analyte, allowing the polymer to rebind the analyte with a very high specificity.

In this work, we have prepared diclofenac-selective molecularly imprinted polymer (MIP) by a simple bulk polymerization process. Simultaneously, the corresponding non-imprinted polymer (REF) was prepared with the same procedure just in the absence of the template molecule, and it was used as a reference.

The rebinding abilities of the obtained materials were evaluated spectrophotometrically through the adsorption of diclofenac in aqueous solution by the same quantity of MIP and REF powders, respectively. The adsorption tests demonstrate that the diclofenac concentration is considerably reduced in the presence of MIP powder. In 10 minutes, 5 mg of MIP was able to remove ~ 90% of diclofenac present in the solution, while only 8% was removed by the REF. In addition, thanks to the imprinting effect, the prepared MIP adsorbs with extreme selectivity its template molecule. This effect was evaluated by testing the adsorption abilities towards different drugs: acetylsalicylic acid and trimethoprim. The results confirmed that less than 10% of these two drugs was adsorbed by MIP.

MIPs traditionally demonstrate their best performance of molecular recognition in hydrophobic organic solvents, this is the main drawback for the application of these materials in water treatment processes. The novelty of this work is the preparation of a MIP able to remove very efficiently diclofenac in aqueous solution with a very high selectivity.

#111 - Selective photodegradation of paracetamol by molecularly imprinted ZnO nanonuts

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Water was taken for granted for centuries, until increasing pollution and reduction of potable water supplies delineated the need to protect our water reserve and develop new technologies to purify water for consumption. Conventional water treatment technologies fail in removing the emergent environmental pollutants, generating the need for the development of novel methods. A class of emerging inorganic materials is that of the semiconductor photocatalyst, because it enables a wide variety of applications including the degradation of environmentally toxic compounds.

In this field, one of the most interesting challenges for the scientific community involved in photocatalysis is the synthesis of new materials with a selective photocatalytic activity for a specific pollutant. Indeed, the photocatalyst does not differentiate between highly-hazardous pollutants and low-toxicity ones. When the photocatalytic semiconductor is irradiated by photons with energy equal to or higher than its band-gap energy, the generated electron-hole pairs can induce on its surface (in contact with water) the formation of reactive oxygen species, such as OH^\cdot , which are directly involved in the oxidation processes that degrade toxic organic compounds, mineralizing them in innocuous CO_2 and H_2O , and cause the death of bacteria, too. Furthermore, when a photocatalyst is used to treat wastewater containing multiple pollutants, the low and/or non-toxic pollutants at high concentration are efficiently degraded, while the highly-toxic organic pollutants at low concentration are hardly removed with less efficiency. To solve this problem, we originally propose molecularly imprinted ZnO nanonuts as new nanomaterial. In this work, ZnO have been imprinted, through a chemical method, with one of the most diffused analgesic-antipyretic drugs: acetaminophen (commonly called “paracetamol”), today considered as an emergent environmental pollutant. Thanks to the accurate performed characterization, the interaction between ZnO and paracetamol has been elucidated. The photodegradation of paracetamol in aqueous solution has been demonstrated under UV light irradiation. The selectivity of the photodegradation process has been additionally investigated thanks to the comparison with the degradation of methyl orange (MO) and phenol, another two common water pollutants. Imprinted ZnO nanonuts have shown a great affinity and selectivity for the paracetamol, being able to degrade all the paracetamol present in the aqueous solution in 3 hrs.

#112 - Multifunctional materials based on GO-PHEMA ZnO for pollutants adsorption and photodegradation

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Due to rapid population growth and intensification of agricultural and industrial activities, a diverse array of hazardous pollutants is progressively entered in the aquatic system. Particularly, persistent organic contaminants such as pesticides, solvents, dyes, detergents and industrial chemicals, constitute a pressing ecological problem that poses a great threat to human health. Water purification methods applied in the last decade involve high operating costs and could generate toxic secondary pollutants into the ecosystem. An eco-friendly and definitive process to eliminate contaminants from water via mineralization, involves photocatalytic approaches acted by polymer supported photocatalysts. Here, the design of new hybrid nanocomposites based on poly (2-hydroxyethylmethacrylate) (PHEMA) graphene oxide (GO) cryo-sponges, wherein ZnO nanolayers have been deposited, is reported. Atomic layer deposition (ALD) at low temperature is specifically selected as deposition technique to stable anchor ZnO molecules to the pendant polymer OH groups. Furthermore, to boost the PHEMA cryo-gel adsorption capability versus organic dyes, GO is added during the synthetic procedure. The morphology, the crystallinity, and the chemical composition of the samples were deeply investigated by scanning electron microscopy (SEM), X-ray diffraction analyses (XRD), Fourier transform infrared spectroscopy (FTIR) as well as thermogravimetric analysis (TGA). Swelling properties and adsorption kinetics models of the hybrid materials were also evaluated. Finally, the adsorption and photocatalytic performance were tested and compared for all samples by using methylene blue (MB) as simulant dye. Particularly, the adsorption efficiency of ZnO PHEMA and ZnO PHEMA GO nanocomposites, as well as they *in situ* regeneration via photocatalysis, render such devices very appealing for advanced wastewater treatment technology.

#113 - Removal of chromium (VI) from aqueous solutions by grafted chitosan

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Chitosan was deposited on cotton gauze at different add-ons (0.02, 0.05 and 0.10 g chitosan/g cotton) by UV-curing in order to improve its stability in water. Obtained samples were employed for the adsorption of hexavalent chromium ions (Cr(VI)) from aqueous solutions at pH of 3.0 and temperature of 20°C . In this study, kinetic model (Lagergren's pseudo-first-order or Ho's pseudo-second-order) and isotherm adsorption (Langmuir, Freundlich, Dubinin-Radushkevich and BET) were determined. Results showed that the adsorption of chromium occurred by a kinetics of pseudo-second-order with an adsorption isotherm type II. The most probable energy of adsorption, from Dubinin-Radushkevich isotherm model, foresees that a physisorption was achieved by hydrogen bond interactions between chromium ions and protonated amino groups. In addition, the adsorption capacity of chromium ions on grafted chitosan (56 - 103 mg Cr(VI) /g chitosan) was higher than that reported in literature for pure chitosan (8 - 24 mg Cr(VI) /g chitosan). In this way, it was demonstrated that a higher adsorption can be reached with lower amount of chitosan by UV-curing. Finally, the specific surface area occupied by chromium ions was estimated by means of the adsorption capacity of BET model.

#114 - Synthesis, characterization and applications of shape controlled anatase nanoparticles

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The synthesis of TiO₂ nanoparticles (NPs) with well-defined morphology and size is fundamental for the development of advanced nanomaterials in various application fields. Synthetic routes were developed for bipyramidal TiO₂ facet-controlled anatase NPs with low truncation along the c-axis and acicular morphology, through hydrothermal treatments of aqueous solutions of Ti^{IV}(triethanolamine)₂ [1,2] complex. The shape control agents used were pH, temperature and triethanolamine. Bipyramidal TiO₂ anatase NPs (that largely expose (101) surfaces) with low truncation along the c-axis were produced. Through a careful experimental design the influence of many process parameters on the synthesis outcome (size, shape and polydispersity), a predictive soft model was developed that is able to predict reasonably well the synthesis outcome. The synthesis of TiO₂ anatase nanosheets which presents high percentage of (001) facets are carried out with a solvothermal synthesis using hydrofluoric acid as capping agents [3]. Bipyramids and nanosheets were then tested against different organic substrates (phenol, melamine and formic acid) that undergo three different photo-oxidation mechanism on TiO₂ NPs. Moreover, they were tested in the production of H₂ by formic acid photoreforming using Pt as co-catalyst. The results allow to rationalize the effect of the shape (and shape controllers) on the photocatalytic activity of TiO₂ anatase nanoparticles.

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#115 - DESIGN OF CELL INSTRUCTIVE PLATFORMS AND DRUG DELIVERY SYSTEMS BY ELECTROFLUIDODYNAMIC TECHNOLOGIES

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In the last two decades, a large variety of processes and tools has been investigated to design multifunctional platforms with controlled chemical, physical and biological properties suitable for different applications in biomedical area (i.e., tissue repair and regeneration, cancer therapy, therapeutic and teragnostic use) [1]. Among them, ElectroFluidoDynamic (EFDs) technologies – including electrospinning, electrospraying or hydro dynamic atomization - have raised particular interest by identifying simple fabrication processes able to develop innovative devices with restrained manufacturing costs and high structural/functional complexity [2]. By the interaction with electrostatic forces generated by high voltage electric fields, biomaterials - mainly polymers and composites - can be finely manipulated in different forms for the fabrication of a plethora of 3D platforms with controlled micro/nanostructure/texture (i.e., scaffolds/ μ -scaffolds, mono or multicompartement micro-gels, particles or capsules, micro- and nano-structured coatings) to more efficiently address *in vitro* and *in vivo* cell activities [3]. Indeed, EFDs allow to produce fibres [4] and/or particles [5] at micro- and/or submicro-metric size scale through a rational optimization of process conditions, also offering the opportunity to include biopolymers (i.e., proteins [6], polysaccharides [7]) and/or bioactive molecules (e.g., growth factors [8], chemo- and therapeutic drugs [9, 10]) able to promote specific interactions among cells and local microenvironment. Herein, it will be proposed an overview of recent advances in the design and fabrication of bio-inspired platforms designed via EFDTs, mainly emphasizing their suitability for tissue engineering and drug delivery applications.

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#116 - Nanostructured silicon nanowires and electrospun polymer nanofibres as novel glial interfaces to modulate astrocytes biophysics.

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Introduction. Exploiting the potential of nanostructured material to interface and modulate molecular and functional properties of cells in the central nervous system will be critical to increase our understanding of brain function and dysfunction. Astrocytes, non neuronal cells of the brain, expressing ion channels and aquaporin (AQP) are key players in brain physiology and pathology. Nonetheless, the astrocyte/material interaction needs to be considered in engineering implants targeting the brain, as they are the first cells reacting to the presence of implants in the brain. However, the knowledge on astrocytes/materials interaction provided *in vitro* are limited by the fact that astrocytes, in culture, lose the morphological and functional properties displayed *in vivo*. **Aim.** Our goal is to define and validate innovative nanostructured materials interface based on gold coated silicon nanowires (Au/SiNws) and electrospun nanofibers made of biodegradable polymers such as polycaprolactone (PCL), as substrates to generate *in vitro* models where astrocytes differentiate and display an *in-vivo*-like morphological and functional phenotype. Nonetheless, the possibility to modulate and record astrocytes electrophysiological properties on the interface and by the devices is explored.

Methods and Results. Cell viability assays indicate that Au/SiNws and PCL nanofibers enable strong astrocytes adhesion and growth without need of additional coating with values comparable to those obtained by using glass coverslips treated with Poly-D-lysine. Fluorescent and confocal imaging, Scanning Electron Microscopy and Atomic Force Microscopy reveal that astrocytes respond to the 2D and 3D substrate topography by morphological differentiation and elongation sprouting from the cell body. SEM analyses revealed intimate contact of astrocytes with nanostructure. Immunofluorescent analyses showed that the cells differentiation was not due to inflammatory gliotic reaction suggesting a positive interaction between the material and the cells. Confocal imaging showed that electrospun PCL nanofibers enable astrocytes process alignment along the nanofibre with F-actin fibre alignment and vinculin polarization. Nonetheless PCL-based composites don'tt alter functional properties of astrocytes, investigated by patch-clamp. Interestingly, the differentiation promoted by Au/SiNws was accompanied with higher expression of ion channels and AQP4 at the astrocytic endfeet.

Conclusions. Our results validate PCL nanofibres and Au/SiNws as novel glial interfaces that enable the growth, differentiation and polarization of astrocytes *in vitro*. The glial interfaces are also capable of modulation and recording of functional properties of astrocytes, representing the first class of devices enabling to dialogue with non excitable cells.

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#117 - Eumelanin based micro fibers as biointerface to promote SH-SY5Y neuroblastoma cell growth and maturation

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The search for tissue-engineered scaffolds capable to produce 3D functional tissues suitable for implantation is gaining increasing interest in view of possible application in neurodegenerative disorder therapies. Scaffolds are required to provide i) mechanical support for growing neurites, ii) prevention of ingrowth of fibrous scar tissue in the regeneration phase iii) biological signals to direct the axonal growth cone to the distal stump. Eumelanins, the black insoluble pigments of human skin, eyes and substantia nigra (neuromelanin), stand today as a unique source of inspiration for the design and implementation of soft biocompatible multifunctional materials for bio-optoelectronic devices.

The availability of access routes to 3D eumelanin architectures provides a novel strategy to realize tissue-engineered scaffolds for neuronal cell growth and control, combining mechanical support and biological signals. Herein, we present a detailed investigation of SH-SY5Y neuroblastoma cell growth on a novel eumelanin based biointerface. Scaffolds fabrication relied on electrospinning spin coating and solid-state polymerization processes and biological analysis involved a human derived cell line from neuroblastoma. Eumelanin microfibers proved capable to support biological response in terms of cell survival, adhesion and spreading and to promote cell differentiation toward a more mature neuronal phenotype as confirmed by GAP-43 expression over the culture.

#118 - Development of a new bio-compostable multilayer for antioxidant food packaging

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The development of new bio-compostable materials is attracting a great attention in the field of food packaging. However, the main drawback of biodegradable films is the low barrier they offer against external agents that can thus easily degrade the food, limiting their use to a small number of products. To overcome this issue, we developed a new multilayer film bio-compostable with excellent oxygen barrier proprieties, allowing to increase the shelf life of products without the need to add any preservative agents to the food's recipes. The oxygen barrier is obtained by including in the multilayer film system a layer of water based gel activated with ascorbic acid. The active gel is deposited on a biodegradable Poly(lactic acid) (PLA) film, in a dedicated film-forming machine developed for this purpose. The machine allows a pre-industrial production and includes an in-line plasma source to enhance the hydrophilicity of PLA allowing uniform coating. The main effect of plasma treatment is to increase the number of alcohol and methyl groups on PLA surface, enhancing the contact angle and guaranteeing a perfect coating with the active gel solution. In order to monitor the efficiency of the multilayer fabrication process of the here presented packaging, we developed a sensor based on a conductive polymer, to monitor the activity of ascorbic acid. The sensor is low cost and has a simple read out and it can be easily integrated in-line in the film-forming machine.

The final multilayer of PLA is totally biodegradable and with high oxygen barrier, perfectly implementing a green food packaging.

#119 - KERATIN-HYDROTALCITES HYBRIDE CAST FILM AND ELECTROSPUN MEMBRANES FOR CONTROLLED DRUG RELEASE AND WOUND HEALING

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Keratin is the most abundant fibrous protein, in nature, being the major component of hair, wool, horns, nails and feathers. This protein can be extracted, at low cost, from renewable sources, such as waste by-products of the dairy, butchery and textile industries (coarse wool not fit for spinning, pig hair and feathers). In particular, wool keratin is a biodegradable and biocompatible polymer, with molecular weights ranging from 28 to 50 kDa, and possesses the amino acid sequences responsible for cell adhesion (Arg-Gly-Asp and Leu-Asp-Val); this is why it is an excellent candidate for applications in the biomedical field, particularly in wound healing and drug delivery [1]. Moreover, due to its chemical and physical characteristics, this protein can be transformed into bio-matrices with different porosity and specific surface, functional in the drug release and tissue regeneration processes. A great aspect is the possibility to functionalize these matrices so that they release drugs in a controlled manner. In this work, hybrid keratin and hydrotalcite systems have been prepared for controlled drug release. Hydrotalcites (HTlc) are biocompatible hydroxides [2] with a double layer, whose positive charge is balanced by anions that are reversibly interposed between the layers. In particular, Zn/Al mixed hydrotalcites were synthesized and intercalated with diclofenac sodium salt, useful both to alleviate pain and accelerate the healing process. The obtained hydrotalcites (HTlcD) were then incorporated into keratin membranes of different porosity, mainly cast film (KF-HTlcD) and electrospun nanofibers (KNF-HTlcD). The keratin and HTlc solutions were rheologically characterized and the obtained bio-materials have been characterized from a structural point of view (morphology, porosity, swelling, etc). In order to evaluate the prepared membranes as transdermal release systems of active ingredients, the diclofenac release tests have been performed under physiological conditions (in phosphate buffer at pH 7.4 and at 37 °C). The release profiles of the hybrid materials were compared with those of films and nanofibers containing the free drug (dispersed in the keratin matrix, without the use of HTlc). Finally, in vitro tests were performed to evaluate the toxicity and ability of the matrices to promote fibroblast cell growth.

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Organic, polymer and hybrid nanostructures, and bio soft materials	Andrea Camposeo
Stimuli-responsive materials	Alberto Credi
Low-dimensional Structures for Nanoelectronics and Nanophotonics	Vittorio Privitera
Chemical Functionalization and Characterization of 2D Materials	Maria Caporali
Stimuli Responsive Bioorganic Materials and Smart Surfaces	Vincenzo Guarino
Advanced Structural Characterization of 2D Materials	Stefano Frabboni

#120 - Eco-friendly Growth and Characterisation of MoS₂ Crystals*Luca Ortolani - CNR IMM Bologna*

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Two-dimensional transition metal dichalcogenides (TMDCs) possess a unique combination of physical properties [1-5], showing great potential for diverse applications such as gas sensing [6], actuation [7], nanophotonics [8], renewable energy devices [9] and electronics [10]. As it has already been proven in the case of graphene, chemical vapour deposition (CVD) provides scalable large area high quality material suitable for optoelectronic applications [11].

In this work, a two-step atmospheric pressure CVD method for the production of 2D MoS₂ crystals is presented, exhibiting controlled and large area growth of single (SL) and few-layered (FL) crystals through the reaction between sulfur vapours and pre-deposited sodium molybdate (Na₂MoO₄) on a Si/SiO₂ substrate. Sodium molybdate, in contrast to commonly used MoO₃, is a non-toxic and environmental friendly water-soluble precursor known as a fertilizer. A controlled and eco-friendly, scalable CVD technique for the production of single and few layer MoS₂ crystals is therefore developed. For low precursor concentrations, isolated single layer MoS₂ crystals, with controllable lateral size were produced. Higher concentrations resulted in continuous single layer films grown in tandem with highly oriented few layer epitaxial domains. The area of the monolayer relative to the few-layer domains can be adjusted.

The significant impact on the optical properties of single layer MoS₂ crystals due to the growth induced strain is also examined. The grown monolayer crystals are found to experience 0.3% biaxial tensile strain relative to the exfoliated ones, while a strain relief of 0.6% is measured when these CVD crystals are transferred to plastic substrates. The correlation of photo luminescence and Raman spectroscopies and the relative high level of mechanical stain induced by growth and transfer enabled an indirect measurement of the deformation potential of the direct optical transition of MoS₂ under biaxial strain, indicating a significant impact of the fabrication method on the optical properties of SL-MoS₂.

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#121 - Growth and characterization of Single Layer Transition Metal Dichalcogenides on Au(111)*Daniel Lizzit - Elettra Sincrotrone Trieste S.C.p.A*

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Transition Metal Dichalcogenides (TMDs) and in particular MoS₂ and WS₂ have been demonstrated to be excellent candidates for electronic devices based on new concepts thanks to the coupling between spin and valley degrees of freedom. This is an intrinsic property of the single layer (SL) TMDs due to inversion symmetry breaking and thanks to the strong spin-orbit coupling of the heavy transition metals (Mo or W) in these SL TMDs. However, in order to investigate the fundamental physics behind these materials and to exploit them for practical applications, SL TMDs with a single domain orientation, that is without mirror domains, high quality and large area are demanded.

Here we present a successful synthesis method based on physical vapor deposition, consisting in dosing Mo or W in H₂S atmosphere onto Au(111), and provide an in-depth characterization of the synthesized SL TMDs through different surface science techniques. Synchrotron radiation based photoelectron spectroscopy with high resolution (HR-XPS) or in the fast modality (fast-XPS) were used to characterize the growth. In particular fast-XPS was instrumental to optimize the growth parameters which turned out to be different for MoS₂ [1] with respect to WS₂[2]. Photoelectron diffraction was then employed to find the structural parameters of the SLs and to unambiguously determine their single orientation character and the relative alignment with respect to the underlying substrate. Scanning Tunneling Microscopy (STM), Low Energy Electron Diffraction (LEED) and Microscopy (LEEM) added further insight into the extension of the SLs and the structural order at the atomic level.

Our results prove that large area SL TMDs with high structural quality and a single domain orientation can be grown in contrast with current chemical vapor deposition techniques that produce mirror twin domains leading to the formation of domain boundaries and dislocations.

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#122 - CVD Growth of Transition Metal Dichalcogenides Centimeter Scale Films

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Technological applications exploiting optoelectronic properties of Transition Metal Dichalcogenides, TMDs, (e.g., WS₂ and MoS₂) need synthesis methodologies able to deposit TMDs as a few layer continuous film with homogeneous thickness. The thickness control is needed due to the strong thickness/band structure correlation in TMDs that provides an indirect-to-direct bandgap transition when going from bulk to monolayer form. Currently, WS₂ and MoS₂ films are typically deposited by two-step growth based on the physical deposition of the metal oxide (i. e, WO₃ and MoO₃) and the subsequent thermal treatment with sulfur. Although the two-step approach can lead to high quality TMDs crystals, the growth of continuous films results challenging.

We propose a one-step growth methodology for the deposition of WS₂ and MoS₂ that exploits volatile metal precursors for the deposition of few layer continuous films on the centimeter scale with a high substrate throughput. A full optical (Raman, Photoluminescence, ellipsometry), structural (FE-SEM), and electrical characterization (mobility, transport gap) of the deposited TMDs film is provided. The effect of post-growth chemical treatment on the physical properties of WS₂ and MoS₂ films is also presented.

Acknowledgments

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#123 - Optimized pathways for obtaining epitaxial graphene on cobalt

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Graphene grown on ferromagnetic substrates has the potential to be used for the realization of spintronic devices, acting as a conductive channel, into which spin-polarized electrons are injected from the ferromagnet support. For this reason, the study of the growth and the electronic structure of the graphene-metal interface is the prerequisite for any practical application.

Here, we characterized the temperature-dependent CVD growth of graphene on Co/W(110) by means of low energy electron and photoemission electron microscopy (LEEM/PEEM). At lower temperatures (350-500°C) the graphene is defective. It grows predominantly epitaxial, though rotational domains with varying azimuthal alignments are also present (Gr_{def}). For this phase LEED shows a (1x1) structure as well as an almost continuous diffraction ring. In addition, the C 1s XPS spectra indicate the presence of

defects in the graphene network along with carbide components at lower binding energy. At higher growth temperatures, instead, (500-600°C), the hot catalytic surface favors the formation of a graphene layer having several rotational domains (Gr_{mis}).

We report that, starting from these two heterogeneous structures formed by different growth conditions (Gr_{def} and Gr_{mis}) it is possible to obtain a single phase epitaxial graphene through a recrystallization process. This is confirmed by the sharp (1x1) LEED spots, in registry with the underlying Co substrate, as well from the reduction of the carbidic components and an increased sharpness of the graphene peak, as observed by XPS. *In-situ* LEEM measurements of the recrystallization process, which takes place via a moving precursor phase, allowed us to calculate the activation energy in the two distinct cases, while XPEEM measurements were used to characterize the chemical composition of this precursor.

#124 - CVD synthesis of graphene on porous stainless steel

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Until now, there have been few studies into the synthesis of graphene on stainless steel by Chemical Vapour Deposition (CVD), despite the fact that it shows promise for applications such as anti-corrosion coatings [1] and energy storage [2]. In particular, for porous stainless steel substrates, the one study available in the literature [3] shows an unusual, textured structure rather than the homogeneous graphene film typically observed for graphene foams [4].

In this study, we demonstrate the growth of homogeneous, high quality multilayer graphene films on porous stainless steel substrates using a CVD process that does not require coating with an additional catalyst material such as nickel or copper. The thickness of the coating is tunable based on the deposition time and concentration of carbon precursor. We discuss the critical points in the process, shedding light on the growth mechanism. In particular, the importance of dissolved carbon in the substrate material is highlighted: in two samples with otherwise identical elemental composition, the resulting coverage of graphene is very different.

Finally, an example application of these coatings is demonstrated in the enhanced evaporation of solvents through porous stainless steel media in the presence of graphene and graphene post-treated by oxidation. In the framework of the Zero Gravity Graphene - Satellite Heat Pipes experiments, one such sample was tested in microgravity during parabolic flight, demonstrating significant improvements in evaporation rate over similar samples without graphene. This has the potential to vastly improve pumpless heat transfer systems typically used for cooling electronic components, in particular in space vehicles and satellites.

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#125 - Tailoring topological states in silicene using different halogen-passivated Si(111) substrates

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We propose the halogenated Si(111) surface for growing topological phases of silicene [1] and other 2d materials, by virtue of density functional theory (DFT) and tight-binding (TB) calculations. The van der Waals interaction between the halogen and silicene is weak enough not to perturb the Dirac-character of the silicene band structure but it is strong enough to guarantee good adhesion and immobilization of silicene on the substrate.

Our results show that the Dirac character of low energy excitations in silicene is almost preserved in the presence of silicon substrate passivated by various halogens. Nevertheless, the combined effects of charge transfer from suspended silicene into the substrate, stretching of bonds between silicon atoms, and symmetry breaking which originates from van der Waals interaction with the substrate, result in a gap E_{g1} in the spectrum of the embedded silicene. We further take the spin-orbit interaction into account and obtain its strength and the resulting enhancement in the gap E_{g2} . Both gaps which contribute to the total gap, vary significantly when different halogen atoms are used for the passivation of the Si surface and for the case of iodine, they have very large values of 70 and 23

meV, respectively.

To examine the topological properties, we extracted an effective TB hamiltonian from our DFT calculations and our results based on Berry curvature calculated along the path connecting the two K points, and Z^2 invariant reveals that silicene on halogenated Si substrates has a topological insulating state which can survive even at room temperature for the substrate with iodine and bromine at the surface.

Similar to the free standing silicene, by applying a perpendicular electric field and at certain critical value which again depends on the type of halogens, the gap closes and silicene undergoes a transition to a trivial insulating state. As a key finding we see that the presence of halogenated substrate except for the case of fluorine, enhances the robustness of the topological phases against the vertical electric field and most probably other external perturbations.

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#126 - Synthesis of corrugated C-based nanostructures by Br-corannulene oligomerization

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The structure and electronic properties of carbon-based nanostructures obtained by metal surface assisted synthesis is highly dependent on the nature of the precursor molecule. Here, we report on a combined scanning tunneling microscopy, soft X-ray spectroscopy and density functional theory investigation on the surface assisted polymerization of Br-corannulene at Ag(110) and on the possibility of building a mesh of π -conjugated polymers starting from buckyball shaped molecules. Indeed, the corannulene units form one-molecule-wide ribbons in which the natural concavity of the precursor molecule is maintained. These C-based nanostructures are corrugated and merge in a covalent network on the surface.

#127 - Additive manufacturing technologies for optical materials

Dario Pisignano (I) - University of Pisa and CNR-NANO

Additive manufacturing technologies, i.e. so-called 3D printing, are rapidly introducing new paradigms for the design and fabrication of non-planar and complex optical and photonic devices. These technologies rely on the layer-by-layer fabrication of 3D objects, starting from their digital model. However, the production of truly 3D optical structures is still challenging in terms of the transparency, resolution, and doping possibilities that can be achieved in the ultimate materials. Here we report on 3D-printed materials and manufacturing technologies specifically addressed to photonics, particularly on nanocomposites where active organic chromophores are embedded and 3D shapes obtained without function loss. These components are highly promising building blocks of 3D optical switches and engineered light sources. The research leading to these results has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement No. 682157, "xPRINT").

#128 - Multifunctional Bio-Soft Materials for Photoactivated Therapies

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The achievement of soft-materials able to release therapeutic species in a photo-controlled fashion is a major challenge in the burgeoning field of nanomedicine.^{1,2} Light is in fact a powerful tool for the introduction of bio-active agents in a cellular environment, mimicking an "optical microsyringe" with an exquisite control of three main factors, site, timing and dosage, which are determining for the therapeutic outcome.³ Moreover light-triggering is biofriendly and offers the additional advantages of not affecting important physiological parameters such as temperature, pH and ionic strength. Singlet oxygen (¹O₂) and nitric oxide radical (NO) are two main cytotoxic species, which can be photogenerated by means of suitable photoprecursors. Common to ¹O₂ and NO is the capability to attack biological substrates of different nature (i.e., lipids, proteins, and DNA), representing multitarget therapeutic agents and avoiding Multiple Drug Resistance problems encountered with several conventional drugs often target-specific. Moreover, due to their short half-life and lack of charge, both ¹O₂ and NO radical diffuse in the cellular environment over short distances without inflicting systemic side effects common to general anticancer drugs. For all these reasons, the combination of ¹O₂ with NO has received growing attention in the last few years with the exciting prospect to tackle cancer diseases.⁴ In our laboratories, we have been working on the design and fabrication of a number of engineered, fluorescent soft nanoconstructs able to photogenerate ¹O₂, NO or both under either one- or two-photon excitation. This contribution illustrates some of the most recent and representative examples including polymer, silica and micellar nanoparticles, hydrogels and thin films highlighting the rationale design and their potential relevance in anticancer and antibacterial therapeutic applications.

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#129 - In situ polymerization approach to hybrid 2D black phosphorus/polymer materials: a novel strategy for optoelectronic device fabrication

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The synergic effect due to chemical interactions between polymer and nanostructured fillers is the key parameter to provide materials with excellent performance and widespread applications. Improvements in mechanical, thermal, and barrier performance as well as new light-responsiveness or antimicrobial and antifouling features can be obtained by dispersing different 2D nanofillers at the nanoscale level. With reference to the particular class of 2D nanofillers used for optoelectronic devices (graphite and transition metal dichalcogenides), the specific interactions with a polymer matrix can be used to improve the performance of devices and to protect the nanostructures from aging.

Black phosphorus (bP) has been extensively investigated for both electronic and photonic applications. However, the difficulty in engineering large scale exfoliation procedures and the intrinsic instability of exfoliated bP towards both moisture and air has so far overshadowed its possible applications. Here, polymer-based hybrid materials containing dispersed black phosphorus nanoflakes (bPn) are prepared, and their structural characteristics analysed and compared, to evaluate the bP dispersion degree and the effectiveness of bPn interfacial interactions with polymer chains aimed at their environmental stabilization. In particular, the polymethyl methacrylate (PMMA) passivation results particularly effective for the hybrid material prepared by polymerization in-situ of MMA, after the direct liquid phase exfoliation in the monomer (without solvent and by operating in ambient conditions). The procedure yields hybrids where the bPn, even if with a gradient of dispersion (size of aggregates), preserve their chemical structure from oxidation and even after UV exposure.

The feasibility of this methodology, capable of efficiently exfoliating bP by protecting its structure, is verified using different vinyl monomers: styrene (S) and N-vinylpyrrolidone (NVP) and even by building PS-block-PMMA copolymers. The PMMA-based hybrid is used to design a device without the need of a glove box in any stage of the fabrication, where the nanoflakes show resistance and mobility comparable with electronic-grade liquid phase exfoliated bP. This result proves that the methodology here realized provides hybrid materials as suitable platforms for devices fabrication in the field of optoelectronics.

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#130 - Novel 3D graphene and cyclic-polyporphyrins hybrid materials for photocatalytic applications

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The combination of organic photosensitizers with graphene-based materials has become indeed a hot topic in water remediation. We demonstrate a novel innovative approach that consists in combining properties of graphene foam (GF) and cyclic-porphyrin polymers in a freestanding device. The cyclic chains were dissolved in different solvents and used to impregnate via bath deposition graphene templates. Depending on the nature of the solvent, polymer coats differently the graphene substrates determining peculiar SEM and AFM data. Assembly by using DMF promotes a direct and extensive contact between the graphene and the photosensitizer polymers through the instauration of non-covalent interactions at the materials interface. At the same time, the polymer coating confines graphene materials to the direct exposure of light, dyes and OH• radicals, which drastically reduce the photocatalytic efficiency (PCE). On the other hand, the choice to use sterically hindered cyclic-polyporphyrins as photoactive system, offer several advantages if compared to other systems reported in literature [1]. The photocatalytic degradation tests were carried out by using Methylene Blue (MB) and Rhodamine B (RhB) as simulating dyes. We highlighted that 400 mg of polymers supported on 6 mg of GF explicated an outstanding PCE with good recyclability capabilities under visible-light exposure [2].

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#131 - The role of the constrained amorphous interphase on physical properties of bio-based polymeric materials

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The classical description of semi-crystalline polymers that considers only two distinct phases, has been replaced in recent years by a more complete one, which takes into account also the constrained amorphous nanophase present at the amorphous/crystal interface. This micro- and nanophase structure is determined by competition between crystallization and vitrification, which leads to the development of different amorphous regions, which, due to different distance from the crystalline domains, can exhibit different molecular dynamics. A detailed description of the micro- and nanophase structure of semi-crystalline polymers is decisive for a full understanding of the physical properties of these materials. Indeed, it has been recently proved that many macroscopic properties of semi-crystalline polymers, as for example mechanical and barrier properties, are defined not only by the degree of crystallinity, but also by the percentage of constrained amorphous nanophase. The quantification of this nanophase is therefore a crucial step in the characterization of a polymeric material, since different processing conditions affect in different ways the evolution of the crystalline and amorphous fractions.

The subject of the presentation will be the evolution, during solidification, of the constrained amorphous interphase in some bio-based polymers, as poly(l-lactic acid) (PLLA) and poly(3-hydroxybutyrate) (PHB), which, owing to their biodegradability, can be utilized for a variety of applications. In addition, the contribution of the constrained amorphous nanophase to physical ageing of PLLA, as well as to the mechanical properties of PHB will be presented and discussed.

#132 - In Vivo Fabrication of Fluorescent Conductive Microfibrils

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Conductive polymers are very attractive for biomedical applications. Their responsiveness to electrical stimulation found application in nerve regeneration strategies (i.e. polypyrrole), enhanced neuronal growth (i.e. by polypyrrole functionalized with laminin), tissue regeneration through artificial fibrillar components of extracellular matrix. Often their broad use is hampered by low biocompatibility and biodegradability, lack of recognition elements for endogenous components, thus alternative strategies may rely on improvement of fibrillar proteins properties *in situ*. In this direction, the fluorophore dithienothiophene-S,S-dioxide (DTTO) is able to spontaneously enter human and mouse fibroblasts and become incorporated into collagen quaternary structures (including triple helical domains) giving rise to fluorescent and conducting fibrils, without causing adverse effects on cell viability and proliferation. In order to translate to an **in vivo system**, we employed the freshwater polyp *Hydra vulgaris*, which structural simplicity resembles a living tissue, without organs and central nervous system. By challenging living polyps with low amount of the fluorophore dithienothiophene-S,S-dioxide (DTTO) we demonstrated the stable incorporation of this thiophene based molecule into ordered supramolecular structures giving rise to microfibrils. Electronic force microscopy showed electrical conductivity and circular dichroism analysis confirmed the presence of proteins within the fibrils. Beside the possibility of naturally engineering endogenous components by self assembly of synthetic moieties and native proteins, this approach opens the path to a sort of 'live animal factory' for the production of innovative biomaterials.

#133 - Responsive soft materials made by supramolecular self-assembly

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Self-assembly is emerging as a superior method to prepare adaptive and responsive nanomaterials. The structure and function of these materials is entirely determined by the dynamic and weak interactions of the constituent molecular “building blocks” of the material. Since the inherent interactions are weak, these versatile materials readily respond to even small changes and stimuli in their environment. Moreover, these materials are biomimetic and contain large amounts of water, so that application in biomedical technology can be foreseen.

This lecture will highlight self-assembled nanocontainers based on cyclodextrins that respond to various external stimuli. Amphiphilic cyclodextrins form bilayer vesicles in aqueous solution and the surface of these vesicles can be functionalized using host-guest chemistry. Shear-thinning hydrogels result if the cyclodextrin vesicles are mixed with adamantane-functionalized polymers, which act as supramolecular cross-linkers. Photo-triggered payload release from supramolecular hydrogels is enabled by incorporation of azo-modified peptides. Polymer-shelled vesicles and polymer nanocontainers are obtained if the cyclodextrin vesicles are decorated with adamantane-terminated poly(acrylic acid), which can be cross-linked with diamines. Recently, we have also shown that this polymer shell is redox-responsive if the cross-linker contains a disulfide. The resulting nanocontainers can deliver cargo into cells. Magneto-responsive soft materials are obtained by supramolecular incorporation of magnetite nanoparticles into vesicles and gels.

Furthermore, the lecture will include several examples of the transfer of the concept of stimulus-responsive assembly to nanoparticles and nanofilms.

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#134 - New photochromic materials based on a tricyclophosphazene core functionalized with six azobenzene units substituted with alkyl groups

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The development of new photochromic materials that can be reversibly interconverted by light between forms with different physico-chemical properties is of high interest for separation, catalysis, optoelectronics, holography, mechanical actuation, and solar energy conversion.

Here we report the synthesis and characterization of a new family of photochromic compounds based on a tricyclophosphazene core functionalized with six azobenzene units substituted in the para position with alkyl groups of different bulkiness. A comprehensive photophysical characterization was performed both in solution and on thin solid films prepared by spin coating, drop casting and spray coating. Quantum yield of photoisomerization at different irradiation wavelengths and thermal back reaction kinetic parameters were measured in different solvents and for different film deposition methodologies. All materials display a clean photoinduced *E* -> *Z* isomerization of the azobenzene units in solution, albeit with a strong dependence of the fatigue resistance on the nature of the solvent. UV-Vis absorption spectra and polarizing optical microscope images recorded on solid thin films revealed that, independently from the deposition methods, both the bulkiness of the substituents on the azobenzene arms and the thermal history of the film strongly affect the degree of crystallinity thus influencing the solid-state photochromic properties. Bulky substituents disfavor crystallinity and result in glassy amorphous films that display a higher efficiency in the *E* -> *Z* photoisomerization reaction while films from materials with less bulky substituents form crystalline films in which the lower *E* -> *Z* photoconversion efficiency is accompanied by an isothermal phase transition from crystalline to amorphous. The strong correlation between molecular structure and solid-state organization enables an unprecedented fine tuning of the photochromic properties of these materials in the solid state suggesting interesting technological application in the field of light responsive materials.

#135 - Dual-responsive copolymers bearing 2-(hydroxyimino)aldehyde and oligo(ethylene oxide) groups: an example of serial interplay promoted by light.

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2-(hydroxyimino)aldehydes (HIAs) are a class of organic molecules characterized by an aldehyde group adjacent to an oxime moiety.^{1,2} Beyond the interesting properties brought by the conjugation of oxime with CHO, such as a greater acidity than that of simple oximes (pKa 7.7- 9.9) and reversible oxidation potentials for the oximate anion below 0.7 V vs NHE, the light effect is the most intriguing. In fact, two types of isomerization are possible under the effect of the light: the thermally reversible interchange of two configurational isomers E and Z and the irreversible cyclization to cyclobutanol oxime by Norrish-Yang rearrangement.

In our investigation, a monomer encompassing the HIA group in the side chain was synthesized (HIABMA) and then copolymerized with OEGMA₅₀₀ in different ratio (1:1, 3:7, 1:9) by RAFT method. The polymers were obtained with excellent yields (60-90%) and low polydispersity index.³

The thermal behaviour of aqueous solutions of all synthesized copolymers was then investigated and related to irradiation at 350 nm. Cloud Points of copolymers bearing the HIA group are lower with a higher HIABMA/OEGMA ratio. In fact copolymer with ratio HIABMA/OEGMA 1/9 remains clear up to 80 °C, while a ratio 1/1 gives a Cloud Point of 43 °C. After 22 hours of irradiation with a high pressure mercury lamp at 350 nm, around 40% of HIABMA groups are converted to cyclobutanol oxime. This isomerization is sufficient to increase the LCST by 14°C resulting in a serial responsive behaviour. All these results lay the foundation for the development of a new class of multi-stimuli responsive polymers.

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#136 - Azobenzene tetramers derivatives for the development of photoresponsive microporous materials.

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Materials able to change their properties in function of the application of an external stimulus represent one of the main topics of interest with applications in the field of optoelectronics, sensors and catalysis. We recently reported the synthesis of tetramers where four azobenzene units were covalently linked through a central tetrahedral carbon, endowing the molecule with a rigid star-shaped structure. Such molecules showed the ability to assemble into porous crystalline systems, characterized by channels whose size and shape could be controlled by introducing substituents on the azobenzene groups. An outstanding property of these tetramer molecules is the ability to undergo E-Z isomerization of the azobenzene groups in the solid state by irradiating with UV light at 365 nm. A direct consequence of the solid state isomerization was the control over the crystallinity of the material in a reversible way by means of irradiation-thermal annealing cycles. Moreover the porous crystals constituted by tetramers presenting a tert-butyl substituent, were able to selectively adsorb CO₂ in the E state and release it upon light irradiation. Varying the nature of the substituents on the azobenzene groups could bring to new and interesting properties of these molecules, with the ability to further modulate the porosity of the crystals and induce the isomerization by means of visible light irradiation, opening up the range of technological applications of the materials.

#137 - Optical Sensor Based on Redox-Active Tetrazolium / Pluronic Nanoparticles Embedded in PDMS Films

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The fabrication of high sensitive and portable devices for the rapid detection of toxic gases and vapours is of high interest for safety applications. In this sense, redox-switchable molecules are promising candidates for the detection of toxic oxidant chemicals due to their reversible colour change. The in-situ reduction of water-soluble organic molecules in the presence of polymeric surfactants is a simple, cheap and green method for the production of colour switchable nanoparticles. In this work, pluronic F 127 was used as stabilizer for the reduction of 2,3,5-triphenyl-2H-tetrazolium (TTC) into triphenyl formazan (TF). The TTC reduction resulted in the successful production of red-colour nanoparticles with zeta potential closed to zero and hydrodynamic diameters between 138 to 253 nm as hydrophobic dispersion in aqueous media stabilized by the polymeric surfactant. Moreover, these suspensions were embedded in a film of PDMS producing a high homogenous red colour gas-permeable elastomeric film. The latter was exposed to a nitrous vapour

resulting in a fast and complete film decolouration due to the oxidation of TF. This coloured redox-switchable composite is a promising material for the fabrication of cheap and compact optical sensing devices for detection of hazardous volatile chemicals.

Keywords: Organic nanoparticles, Pluronic F-127, green chemistry, PDMS membranes

#138 - Opposite Solvatochromic Effects in a Molecular Spin-Crossover Compound Revealed by Ambient Pressure X-ray Absorption Spectroscopy

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We investigate the solvatochromic effect of a Fe-based spin-crossover (SCO) compound via ambient pressure soft X-ray absorption spectroscopy (AP-XAS) and atomic force microscopy (AFM). AP-XAS provides the direct evidence of the spin configuration for the Fe(II) 3d states of the SCO material upon in situ exposure to specific gas or vapor mixtures; concurrent changes in nanoscale topography and mechanical characteristics are revealed via AFM imaging and AFM-based force spectroscopy, respectively. We find that exposing the SCO material to gaseous helium promotes an effective decrease of the transition temperature of its surface layers, while the exposure to methanol vapor causes opposite surficial and bulk solvatochromic effects. Surficial solvatochromism is accompanied by a dramatic reduction of the surface layers stiffness. We propose a rationalization of the observed effects based on interfacial dehydration and solvation phenomena.

#139 - Dynamics of sessile ferrofluid drops

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Ferrofluids are colloidal dispersions of magnetic nanoparticles in a liquid. The possibility of tuning the morphological and dynamical properties of the ferrofluids, taking advantage of their interaction with the magnetic field, is attracting a lot of attention because of its fundamental implications and wide technological applications.

In this presentation we will present different studies on the microfluidic properties of sessile ferrofluid droplets on open surfaces. First we will show how it is possible to tune the static shape of the ferrofluid drops with the magnetic field (magnetowetting)[1]. It is found that the main wetting parameters (contact angle, contact line length and height of the drop) depend both from the gradient and the strength of the external magnetic field generated by permanent magnets. If the magnetic interaction is strong enough, it may lead to the break-up of the ferrofluid droplets in two or more daughter droplets. We have characterized this phenomenon by changing the nature of the surface and the magnetic interaction [2]. Finally, we will present a comprehensive experimental study of the interaction between gravity driven ferrofluid drops on very slippery oil impregnated surfaces in the presence of a patterned magnetic field. It is found that the drop speed can be accurately tuned by the magnetic interaction and, more interestingly, drops are found to undergo a stick-slip motion whose contrast and phase can be easily tuned by changing either the strength of the magnetic field or the ferrofluid concentration [3].

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#140 - Glass-based photonic structures for photons management*Lam Thi Ngoc Tran (I) - IFN-CNR CSMFO Lab*

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Glass photonics is pervasive in a huge number of human activities and drive the research in the field of enabling technologies. Glass materials and photonic structures are the cornerstones of scientific and technological building in integrated optics. Photonic glasses, optical glass waveguides, planar light integrated circuits, waveguide gratings and arrays, functionalized waveguides, photonic crystal heterostructures, and hybrid microresonators are some examples of glass-based integrated optical devices that play a significant role in optical communication, sensing, biophotonics, processing, and computing. We present some recent results obtained by our consortium in rare earth doped photonic glasses and confined structures, in order to give some highlights regarding the state of art in glass photonics. To evidence the unique properties of transparent glass ceramics we will compare spectroscopic and structural properties between the parent glass and the glass ceramics. Starting from planar waveguides we will move to spherical microresonators, a very interesting class of photonic confined structures. Then we will present 1D-photonic crystals and opals allowing management of optical and spectroscopic properties. We will conclude the short review with some remarks about the more significant applications such as laser action and structural sensing and the appealing perspective for glass-based photonic structures.

The research activity is performed in the framework of COST Action MP1401 Advanced fibre laser and coherent source as tools for society, manufacturing and lifescience (2014-2018) and Centro Fermi MiFo (2017-2020) project. L.T.N. Tran acknowledges Vietnamese Ministry of Education and Training for her PhD scholarship.

#141 - Photoluminescence properties of drop-casted films of silicon nanostructures as grown and after annealing in nitrogen atmosphere*Sonia Freddi - Università di Roma "Tor Vergata" e Università Cattolica del Sacro Cuore*

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In the past few years Silicon nanostructures (SiNNs) are being increasingly investigated in all scientific and technological fields due to their unique properties and their potential to be used for disparate applications, e.g. next generation solar cells, light emitting devices or biomedical sensors. Doping process has been recently explored as a strategy to develop high performance Si NNs-based devices with improved optical properties. In this work, we obtain doping through a high temperature annealing in nitrogen atmosphere. We report on a photoluminescence (PL) amplification obtained upon increasing laser irradiance in drop-casted films of as grown (AG) and 1200°C annealed in N₂ atmosphere multi-sized SiNNs, obtained as a Si nanopowder using an inductively coupled plasma torch technique. Scanning and Transmission Electron microscopy revealed the presence of a high percentage of NWs and nanostructures with Si crystalline core diameter below 5 nm (i.e. the Si exciton Bohr radius). Energy Filtered-Transmission Electron Microscopy images demonstrate that all the SiNNs are embedded in a silicon oxide shell and disclose the presence of a small amount of N in the annealed sample, presence which has been confirmed by X-Ray Photoelectron Spectroscopy and Fourier Transform Infrared measurements. PL emission spectrum presents several peaks and extends from 550 to 1000 nm. Upon increasing laser irradiance, changes occurs in the PL emission spectra. For the AG film, all the PL peak intensities exhibit an exponential growth laser power density dependence, which is not the case for most of the PL peaks for the annealed film. An interpretation of the different behavior is given.

#142 - Space-and-time coherent evolution of spatially indirect excitons: the role of the internal dynamics*Federico Grasselli - Scuola Internazionale Superiore di Studi Avanzati - SISSA*

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Spatially indirect excitons (IXs) are long-lived electron-hole pairs which can be optically excited, accelerated in gate-generated potential landscapes, and annihilated on demand in excitonic circuits based on semiconductor coupled quantum well (CQW) devices.[1]

We performed exact Schrödinger propagation of Coulomb bound electron-hole pairs, simulating IXs coherent transport in several classes of in-plane static and time-varying scattering potentials – wells/barriers, single/double slits, dots/antidots, harmonic – using the Split-Step Fourier method, which fully takes into account the two-body dynamics of the pair.[2]

We find that, even when a weak scattering potential cannot induce internal transitions or dissociation of the pair, scattering is substantially influenced by internal quantum dynamics, and IXs cannot be propagated as a rigid body.

Comparing with commonly used mean-field methods, we show that, depending on the type of scattering potential, dynamic correlations cause 1) renormalization of transmission resonances, 2) strongly enhanced tunneling, 3) appearance of diffraction fringes where single-particle scattering would predict none.

We show that these correlation effects can be accounted for by the phase shifts induced by internal virtual transitions during the scattering process. Hence, we propose a self-energy approach which allows to simulate IXs by the center-of-mass degrees of freedom alone in a parameter-free local energy-dependent potential, [3] with orders of magnitude reduction in numerical load, but insignificant loss of accuracy. We specifically analyse IX propagation in surface-acoustic-wave as well as split-gate potentials and its application as single-impurity probes, discussing recent experiments in light of our calculations.[4,5]

Few-body scattering is a fundamental, yet little studied topic, also in chemical and nuclear scattering. Hence, we propose that coherent propagation of IXs in CQWs might prove an ideal playground to test models of correlation.

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#143 - PHOTON MANAGEMENT IN LOW-DIELECTRIC CONTRAST 3D COLLOIDAL CRYSTALS

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Three-dimensional (3D) inverse opal (IO) Photonic Crystals (PC) are appealing for many applications in photoelectrical conversion, sensors, microfluidic devices, separation and catalysis and to develop highly efficient optical devices based on fluorescence detection.

We present the fabrication and characterization of 3D Er³⁺-activated SiO₂ inverse opals (ErIO) in air. We show that, in spite of the low refractive index contrast, and so in the absence of a complete photonic band gap (PBG), the ErIO spontaneous decay rates (SDRs) are modified with respect to the bulk counterparts (ErR) due to the spatial modulation of the effective refractive index n_{eff} at the nanoscale.

Large and well-ordered crystals of silica ErIO in air, with a concentration 0.3% mol (ErIO03) and 0.5% mol (ErIO05) Er³⁺-were synthesised by the sol-gel method. Closely-packed FCC structure was obtained, at 74% fill-factor, with 300 nm of average diameter of the air-hollows, with (111)-oriented surface facet. The prepared samples ErIO display a green bright color, as resulted from optical Bragg diffraction from the crystal planes. As a reference, the bulk counterparts (ErR03 and ErR05) were also fabricated, transparent and crack-free.

We have characterized the optical, structural and spectroscopic features of ErIO and ErR, by comparing the experimental data with numerical modelling. The PC band structure of ErIO was calculated using plane wave expansion method by *MIT Photonic Bands* software. The density of optical states was derived from tetrahedron method [1].

Reflectance measurements on ErIO show the presence of a photonic stop band in the visible region. Room temperature (RT) photoluminescence (PL) excited at 514 nm exhibits a main emission peak at 1540 nm, with a spectral modification in the case of ErIO. Also, RT PL Er³⁺ decay curves of the ⁴I_{13/2} metastable state showed an increased decay time for the ErIO system. Namely $\tau_{1/e}$ = 10.0 ms and 8.5 ns were obtained for ErIO03 and ErIO05, compared to $\tau_{1/e}$ = 5.0ms and 4.0ms of the respective bulk ErR03 and ErR05.

It is worth to note that in IO with low dielectric contrast and low n_{eff} , SDRs are hardly modified by PBG effect of a large-scale collective periodic resonant structure.

Thus, the experimental modification in SDR is likely to be differently originated and it can be understood by considering the changes produced by the medium, acting as a local cavity surrounding the Er³⁺ ions at the nanoscale. This is confirmed by numerical simulating the ErIO if a virtual cavity model is considered.

We can deduce that the modification of n_{eff} leads to an increase of the radiative lifetime, as observed in other similar systems like Y₂O₃:Eu³⁺ [6] and NaY(MoO₄)₂:Tb³⁺, Eu³⁺.

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#144 - Carbon nanotubes as excitonic insulators

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Fifty years ago Walter Kohn speculated [1] that a zero-gap semiconductor might be unstable against the spontaneous generation of exciton—electron-hole pairs bound together by Coulomb attraction. The reconstructed ground state would then open a gap breaking the symmetry of the underlying lattice, a genuine consequence of electronic correlations. Here we show [2] that this ‘excitonic insulator’ is realized in zero-gap armchair carbon nanotubes by performing first-principles calculations through many-body perturbation theory as well as quantum Monte Carlo. The excitonic order modulates the charge between the two carbon sublattices opening an experimentally observable gap, which scales as the inverse of the tube radius and weakly depends on the axial magnetic field. Our findings call into question the Luttinger liquid paradigm for nanotubes and provide tests to experimentally discriminate between excitonic and Mott insulator.

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#145 - Polariton Hall Effect in Transition-Metal Dichalcogenides

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We analyze the properties of strongly coupled excitons and photons in systems made of semiconducting two-dimensional transition-metal dichalcogenides embedded in optical cavities. Through a detailed microscopic analysis of the coupling we unveil novel, highly tunable features of the spectrum, that result in polariton splitting and a breaking of light-matter selection rules. The dynamics of the composite polaritons is influenced by the Berry phase arising both from their constituents and from the confinement-enhanced coupling. We find that light-matter coupling emerges as a mechanism that enhances the Berry phase of polaritons well beyond that of its elementary constituents, paving the way to achieve a polariton Hall effect.

#146 - Ge-Vn complexes in silicon: a viable route toward room temperature single atom devices

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Single-atom transistors are the ultimate scaling solution for applications in quantum information. Devices based on conventional dopant atoms (As, P) in silicon can operate only at cryogenic temperature due to shallow weakly localized impurity levels. We propose here GeV complexes as good candidates to achieve room temperature single electron transport. These hybrid defects pick up the interesting properties of the vacancy in silicon, which carries deep states in the bandgap, and spatial controllability of the defect by single ion implantation of Ge, as the two combine in a complex at suitable annealing temperature around 500°C.

By means of ab initio Density Functional Theory (DFT) calculation with screened-exchange hybrid functional, we characterize structural and electronic properties of different Ge-Vn defects. We calculate the excitation energies for the addition of electrons to the defect finding deep charge transition levels in very good agreement with experimental data. Moreover, the high localization of these defect-related states and the large on-site interaction allow us to shed light on the transport mechanisms in these systems supporting the interpretation of the features observed in the experimental I-V curves.

#147 - PURE SPIN MAGNETO-ELECTRIC EFFECTS DETECTED BY ELECTRIC FIELD MODULATED ELECTRON PARAMAGNETIC RESONANCE ON MOLECULAR HELICES

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The possibility to operate on magnetic materials through the application of electric rather than magnetic fields - thus with faster, less energy demanding, and more space-confined control - makes the investigation of magnetoelectric effects one of the most active research field in material science.¹⁻⁴ An unprecedented magnetoelectric phenomenon was recently predicted in metal-radical helices.⁵ On one of these systems (a Mn-radical helix), the application of an electric field (E) introduces an energy contribution, which is different in case of parallel or antiparallel alignment of the spins along the helix. In other words, the E field modulates the intra-chain exchange interaction J . Even if this modulation is small, its effect is here reported as observed for the first time by exploiting the sensitivity of EPR in combination with a modulation of the E field. It is in fact well known that one-dimensional spin correlation can induce a significant g -shift even when only a weak anisotropy of dipolar origin is present.^{6,7} By modulating the E field in the EPR experiment a modulation of J is induced, which is reflected in the modulation of the resonance frequency. The symmetry of the observed phenomenon unambiguously confirms its magneto-chiral nature. Our observation opens interesting perspectives, which may be relevant also for the investigation of multiferroic materials.

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#148 - Under submissions

Francesco Scotognella (1) - Under submissions

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Under submissions

#149 - Optical properties of 2D material based photonic structures and of chemical functionalized 2D materials

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Latest achievements in the manufacture of black phosphorus and transition metal dichalcogenide thin layers, from few layers to atomically thin layers, are very useful for applications as electronics, optics, and optoelectronics. I will describe the some optical features of one-dimensional photonic structures containing MoS₂, WS₂ and black phosphorus. The very high real part of the refractive index of these materials allows the realization of this photonic multilayers. Furthermore, I will discuss the optical absorption of chemical functionalized black phosphorus nanodots. A red shift of the absorption is noticeable and such shift can be ascribed to an electron delocalization.

#150 - MODIFICATION OF THE ELECTRONIC PROPERTIES OF GRAPHENE THROUGH DIAZONIUM BASED MOLECULES

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Nowadays, the research on graphene is focused on the possibility to modify the band structure of graphene without a degradation of the charge carrier mobility and the destruction of its basic electronic properties. Pristine graphene, at the K point of the Brillouin zone, is a gapless semiconductor with almost no density of states at the Fermi level [1]. Due to the very small conductivity of graphene in this condition, various approaches are being explored to change the charge carrier concentration such as the direct doping of graphene through the chemical modification, either by the introduction of defects or through molecular adsorption. At the same time, an electronic bandgap in the graphene sheet is mandatory to develop the graphene-based electronic devices. Being simple and scalable, chemical modification is becoming a promising approach to modify the graphene electronic structure [2-4]. The method of chemical modification includes the covalent attachment of aryl based molecules onto the graphene surface [5].

In order to access the consequences of chemical modification on the graphene electronic structure, we carried out photoemission experiments during the steps of the growth procedure. The graphene was chemically modified with 3,4,5-trimethoxy benzene diazonium (TMD). The Angular Resolved Photoemission Spectroscopy (ARPES) measurements performed at Synchrotron of Trieste and the X-Ray Photoemission Spectroscopy (XPS) measurements allowed us to study the electronic structure at the interface and the modification of the electronic properties of the Dirac cone. These results are interpreted on the basis of density functional theory (DFT) calculations carried out on TMD alone, as well as on TMD covalently bonded to graphene. The photoemission results were also supported with the information given by the Raman spectroscopy and Scanning Tunneling Microscopy Measurements (STM).

The talk will be focused on the modification of the electronic properties of graphene induced by the covalent attachment of the diazonium based molecules. The element of novelty is the study of the properties of modified graphene never discussed in the literature for this system.

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#151 - Role of defects and chemical doping on the reactivity of supported graphene layers.

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Graphene (G) is considered one of the most promising materials for the future in many technological fields including – unexpectedly – gas sensing and catalysis. Recently, its possible use as gas sensor has been demonstrated [1] and free standing graphene has been used as a sensing element for the detection of different gases. The high sensitivity (ppm or better) is due to the doping induced by adsorption and depends critically on the reactant species, though the nature of the active sites has still to be fully understood. It is also well established that the chemical activity of graphene based materials can be modified and controlled by doping with hetero-atoms, either of the III and V groups (B, N, P) or –more recently – with metal atoms. Literary data suggest that chemisorption of simple gas molecules on graphene is a process involving defected and/or doped sites. In order to clarify this issue, we performed a HREELS and XPS study on the reactivity of pristine, doped and defected G supported on different metals towards CO adsorption. By comparing the results obtained on the different samples, we succeeded in determining the role of the intrinsic doping induced by a strongly interacting substrate, the role of defects introduced in the G layer in form of single vacancies and the effect of the presence of hetero-atoms of one (N-doping) or two species (B-N-doping).

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#152 - High pressure structure and chemistry of layered phases of Phosphorus

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Phosphorus is a key element for chemistry, physics, biology and Earth and planetary sciences [1], that exists in several allotropes with diverse properties. In the recent years, a great interest has grown in the scientific community towards the synthesis, stabilization and functionalization of Phosphorene, a promising 2D platform material obtained from the exfoliation of layered crystalline black Phosphorus (bP) [2]. In this perspective, the layered phases of bP are of special interest, particularly orthorhombic A17, which is the stable allotrope of the element at ambient conditions, and rhombohedral A7, obtained by room temperature compression of A17 above ≈ 5 GPa. On further compression above ≈ 11 GPa, the A7 allotrope was reported to transform into a simple-cubic (sc), non-layered structure. A recent high pressure study [3] has allowed to gain fundamental insight about the mechanism ruling the formation of chemical bonds between P layers, unveiling the existence of an intermediate p-sc structure between the layered rhombohedral A7 and the non-layered simple-cubic phases of P, significantly raising the pressure limit where the layers of P can be observed up to at least 30 GPa, with great implications not only for the phase diagram itself but also for the superconducting behaviour of bP. Furthermore, we have shown [4] that p-sc structure is an intrinsic feature of Phosphorus, that does not depend on the pressure transmitting media, at the same time allowing to derive the Equation of State for A17, A7 and p-sc phases. In addition, the A7 to p-sc transition was demonstrated to follow a first order mechanism. Highlighting the structural relations between A7 and p-sc, we were finally able to solve the apparent contradictions emerging from previous literature data, bringing order to the sequence of HP A7 layered structures in group 15 elements [4]. Besides the structural features, also the study of reactive behaviour of bP is of great interest for what is concerned with its stability. In this framework, we studied the high pressure and high temperature chemistry of Phosphorus in the presence of simple molecular systems (NH₃, N₂). Besides the N functionalization of Phosphorene layers, this kind of studies are relevant to the substantially unexplored chemistry of the low Z pnictogens and to the synthesis of new PN compounds [5].

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#153 - Aza-crown ether functionalized graphene oxide as multifunctional material for gas sensing and cation trapping

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In the wide palette of multifunctional materials, graphene nanocomposites have quickly gained a prominent position. So far, the research focused on graphene and graphene-based materials has led to an extensive assortment of highly performing composites. Graphene oxide nanosheets possess a quite large number of hydrophilic groups, such as hydroxyl, epoxy and carboxyl on the basal plane. Epoxy groups provide some active sites for chemical reactions like the nucleophilic addition. Cyclic aza-ethers can easily react with the epoxy sites on graphene oxide surface resulting in the formation of carbon-nitrogen covalent linkage.

Obtained highly specific surface material, characterized via SEM, TEM, XRD, AFM, FT-IR, Raman and XPS analysis, highlighted polar molecule affinity. In order to take advantage of this feature and to evaluate possible applications as multifunctional material, an easy-to-fabricate and high-sensitivity functionalized graphene oxide-based gas sensor has been achieved by drop-casting deposition onto alumina substrates with interdigitated gold electrodes producing a series of thick-film gas sensors. The material produced is highly stable and capable of detecting, among several gas tested, humidity at room temperature over a wide range of concentrations with fast response and recovery times. Furthermore, the sensing performance are graphene:aza-crown ether rate dependent. The diverse produced devices show a great stability and repeatability over time, confirming that cyclic ether acts as receptor in the sensing mechanism. Produced sensors accomplish sensing performance at room temperature without employing any thermo- or photo-activation energy to reach the full reversibility of the sensing process occurred on the surface.

Moreover, the porous scaffold built by the functionalization, together with the well-known affinity of crown ethers to metal ions, enhanced the possible use of aza-crown ether functionalized graphene oxide for cation trapping application, e.g. pre-concentration of trace amount of metals or filter for water. Remarkable results in this field have been obtained with respect to some heavy metal cations of environmental interest. We also demonstrated the enhancement in performance vs. pure graphene oxide in both tested applications.

The method proposed in this work is quite flexible. Indeed, with an appropriate selection of specific crown-ethers it is possible to tailor molecules with cavities whose size, shape and donor properties would allow the capture of any desired guest in order to prepare a wide range of other crown-ether-GO nanocomposites for gas sensing as well as sorbent materials.

#154 - Synthesis and Raman spectroscopy of a layered SiS₂ phase at high pressures

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Dichalcogenides are known to exhibit layered solid phases, at ambient and high pressures, where 2D layers of chemically bonded formula units are held together by weak van der Waals forces. These materials are of great interest for solid-state sciences and technology, along with other 2D systems such as graphene and phosphorene. SiS₂ is an archetypal model system of the most fundamental interest within this ensemble. Recently, high pressure (GPa) phases with Si in octahedral coordination by S have been theoretically predicted [1] and also experimentally found to occur in this compound [2]. At variance with stishovite in SiO₂, which is a 3D network of SiO₆ octahedra, the phases with octahedral coordination in SiS₂ are 2D layered. Very importantly, this type of semiconducting material was theoretically predicted to exhibit continuous bandgap closing with pressure to a poor metallic state at tens of GPa. I will present on the synthesis of layered SiS₂ with octahedral coordination obtained in a diamond anvil cell at 7.5-9 GPa, by laser heating together elemental S and Si at 1300-1700 K [3]. Indeed, Raman spectroscopy up to 64.4 GPa is compatible with continuous bandgap closing in this material with the onset of either weak metallicity or of a narrow bandgap semiconductor state with a large density of defect-induced, intra-gap energy levels, at about 57 GPa. Importantly, our investigation adds up to the fundamental knowledge of layered dichalcogenides.

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#155 - Polyester-based scaffolds and bioactive hybrid composites with shape memory properties

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Thermally responsive shape memory polymers, capable of deforming from a temporary shape to a permanent shape after an increase in temperature, enable complex mechanical deformation in response to a thermal stimulus and find applications in minimally invasive surgical procedures. Processing shape memory polymers into electrospun mats leads to the realization of smart devices, structured on a micro/nanoscale, of great interest in the biomedical field. In this presentation electrospun scaffolds made of biodegradable and biocompatible shape memory polymers with advanced functionalities, are described focusing on: (i) a 'programmable' scaffold showing a shape memory behavior in the physiological temperature range, and (ii) a bioactive hybrid composite scaffold with enhanced shape memory effect. A shape memory poly(L-lactic acid) (PLLA)-based triblock copolymer was specifically designed to be 'ad hoc' programmed for applications requiring different recovery temperatures, thanks to the concomitant presence of a low melting crystal phase acting as switching segment, and of a high melting crystal phase acting as physical network. Remarkably, it was demonstrated that a straightforward annealing process applied to the crystal phase of the switching element gives the possibility to tune the shape recovery temperature from about 25 to 50 °C, without the need of varying the copolymer's chemical structure. Shape memory poly(ϵ -caprolactone)-based bioactive hybrid composite scaffolds were obtained starting from triethoxysilane poly(ϵ -caprolactone), through a straightforward approach by combining electrospinning process and sol-gel reaction, in the presence of bioactive glass particles (BG 45S5). The results showed that the obtained post-crosslinked electrospun mats had excellent one-way shape memory capabilities, being able to both fix the temporary deformations and to recover the permanent shape up to 100% when heated slightly above the melting temperature. The presence of the Bioglass strongly enhanced the shape memory properties of the polymer, demonstrating the active role of BG in the sol-gel process. Bioactivity of the hybrid composite nanofibers was demonstrated by the deposition of hydroxycarbonate apatite already after one day of immersion in a simulated body fluid solution. Cell culture experiments demonstrated biocompatibility of both investigated systems.

#156 - Stimuli-responsive polysaccharide coating materials by functionalization of chitosan and starch with spiropyran moieties

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Biopolymers have attracted increasing interest in recent times with the aim of producing materials characterized by a low environmental impact and originated from renewable, non-fossil sources. In addition, biopolymers often have multifaceted functional properties related to their peculiar sensitivity to the environment. For these reasons, they are an excellent starting basis for preparing smart responsive organic materials in order to respond to the needs of various applications.

Among polysaccharides, chitin and starch are the second and third most abundant biopolymers on earth after cellulose, respectively. Chitosan, the product of complete or partial N-deacetylation of chitin, is an aminoglucopyran composed of *b*-(1,4)-linked N-acetylglucosamine and glucosamine residues. Starch consists of a mixture of about 10,30% amylose and 70,90% amylopectin, both polymers being made of D-glucoside units with α -1,4- linkages. Amylose, like chitosan, is a linear polymer, while amylopectin is branched with α -1,6-glycosidic bonds occurring every 25,30 units. Each one of these three polymer types was at first regioselectively functionalized at the C6 position with azide groups and then grafted with a N-propynyl-spiropyran (SPCC) by copper(I)-catalyzed azide-alkyne cycloaddition. Materials with different grafting degree were prepared by simply adjusting the SPCC/polysaccharide-azide ratio in the reaction feed.

The newly synthesized materials have been firstly characterized in solution to assess the effects of the coupling of the two components on their properties. In particular, we have studied on one end how these modifications affect the solubility of the biopolymers, on the other hand how the polysaccharide chains affect the photochromic response of the spiropyran groups.

Further to that, solid films of the photo-responsive biopolymers were prepared either by simply casting or via spin-coating and then tested. Their topography has been investigated by means of AFM, revealing a complex morphology that depends on the polysaccharide structure and the modification degree. The spiropyran functionality preserved its photochromic response in the solid films with formation of a magenta colored merocyanine form by exposure to UV light. The UV-Vis kinetics analysis of the color bleaching indicated a very slow thermal recovery of the colored form under room light but a fast recovery by green laser exposure.

The data gathered clearly indicate that these new materials are promising for possible applications in sensor or optoelectronic technologies.

#157 - Antibacterial keratin nanofibers on titanium surfaces for fibroblast adhesion and prevention of biofilm formation

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Periimplantitis and epithelial downgrowth are two of the main conditions related to dental implants failure. In transmucosal implants, the infection onset is due to bacterial adhesion and colonization of the soft tissues in contact with the implant and biofilm formation on the implant surface. The defect in soft tissue sealing and the apically epithelial downgrowth till to the bone level are responsible of bone resorption and implant mobilization promoted by inflammation of the connective tissue. Gingival fibroblasts play an important role in periimplantitis because they are the promoters of the inflammatory process. Moreover, the related inflammatory state is commonly driven also to counteract bacteria implants colonization.

In the present work, a new technology for soft tissue contact is proposed. The first focus of this research is to drive gingival fibroblasts orientation on commercially pure titanium surfaces by means of mechanically produced nanogrooves (0.1-0.2 μm) and to promote their adhesion and proliferation by means of keratin nanofibers deposited by electrospinning. The prepared surfaces have been characterized for their morphology (FESEM), chemical composition (FTIR, XPS), surface charge (zeta potential) and wettability (contact angle). Afterwards, their performances in terms of cells adhesion were compared to mirror-like polished titanium surfaces by means of human primary gingival fibroblasts (HGF). Results revealed that HGF spread was strongly influenced by surface roughness revealing a significant cell orientation along the produced nanogrooves. Moreover, the keratin positive influence on cells adhesion and proliferation was clearly predominant with respect to the stimulus coming from surface topography.

The second aim of this research is to introduce antibacterial properties to the developed technology. So, mirror-polished keratin-coated surfaces were doped with silver (Ag) using different concentrations of silver nitrate as a precursor.

The antibacterial properties of the Ag-doped specimens were tested against a multidrug-resistant *Staphylococcus aureus* biofilm through morphology (FESEM) and metabolic assay (XTT); reduction in viability was significant (480% reduction within 72 h).

Lastly, the cytocompatibility of the specimens was confirmed using HGF, whose viability, spread and matrix deposition were found to be comparable to those of untreated Ti polished controls. Thus, Ag surface enrichment was effective in reducing viability and maturation of *S. aureus* biofilm, without compromising human cell viability.

The strategy thus appears to be very promising to introduce surface features in line with the main requirements for transmucosal dental implants.

#158 - Polymeric micro-patterned film for optical cell layer pacing

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The idea to probe and stimulate biological matter in a non-invasive and contactless way is attracting growing research interests in recent years¹. To achieve this purpose, new optical methods are constantly developed with the aim of transducing light into biological stimuli. In particular, conjugated molecules and macromolecules offer an optimal platform to interface with cells and living organisms thanks to their high optical absorption/emission cross section, chemical synthesis' easiness and relatively low toxicity.

In this work, we are developing an interface with dual functionality. We are studying a simple and fast fabrication method to pattern a blended (poly(3-hexylthiophene)and Polyethylene) polymeric film. This pattern has the purpose to force living cells to organize in a tissue that produce a micro-physiological system; this system will recapitulate the structure and function of native tissue *in vitro*. The polyethylene is responsible for the mechanical structure and properties of the film while the P3HT for the transduction of the light in a biological stimulation^{2,3}.

As alternative we are studying the use of a newly-synthesized azobenzene molecule which are able to stimulate/influence the activity of living cells organized on the micro-patterned film.

In this work we studied the modulation of the contraction rate of cardiomyocytes by visible light. This modulation was monitored via a repeated acquisition of videos followed by a mathematical analysis performed exploiting of an algorithm based on the Motion Vector Field⁴.

Both stimulation and contraction analysis of cardiomyocytes were conducted via optical methods only, although the semiconducting properties of the substrate permits possible applications of such a system in optoelectronics (i.e. bioelectronics).

We are focusing this work on the study of cardiomyocytes and muscle cells in order to produce an artificial tissue for future applications in the robotic, pharmacological and regenerative medicine fields. At the same time the fabrication methods and the stimulation process make it appealing also for different applications (i.e. tissue and neural regeneration).

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#159 - Tattoo Electrode Records Brain Activity

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Tattoo technology is an attractive platform for the development of next generation wearable devices¹. It allows to develop a conformal interface with the human body, thanks to its physical characteristics: low thickness and softness. We've recently demonstrated that Temporary Tattoo Electrodes (TTEs) are able to record electrophysiological signals^{2,3} as electromyography (EMG) and electrocardiography (ECG) on various anatomical district. TTEs are all made by polymers. They adopt temporary tattoo paper as substrate, which have a polymer nanofilm integrated, on top of which PEDOT:PSS is ink-jet printed. Here we show the capabilities of this promising technology in electroencephalography (EEG), in clinical applications. EEG is the smallest and the lowest filtered signal, accessible from the outside of human body, so it's the most challenging scenario in electrophysiology. Gelled Ag/AgCl electrodes are routinely used in EEG despite their disadvantages, mainly related to limited time stability due to gel drying, which impose severe restrictions in EEG applications. TTEs have been thus tested in different clinical conditions, to cover the most of EEG diagnostics. We firstly validated TTE with the recording of alpha waves, the most known brain rhythm. TTEs were also compared with Ag/AgCl electrodes, through Power Spectral Density (PSD) assessment, showing a good match over the whole signal spectrum. TTEs were further evaluated in auditory evoked potentials (AEP) measurements, in comparison with the standard Ag/AgCl electrodes, exhibiting comparable results. Furthermore TTEs' compatibility with magnetoencephalography (MEG) equipment have been performed. EEG/MEG are frequently used in combination and at the best of our knowledge it is the first time that a dry electrode exhibits complete compatibility with MEG.

The successful evaluations of TTEs in the EEG field paves the way for future development of imperceptible alternatives to standard electrodes in clinical practice.

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#160 - Evaluating the role of durotactic migration in the glioblastoma (GBM) tumour microenvironment

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Durotaxis is the directional cell movement in response to a stiffness gradient of the local microenvironment. Its role in cancer biology is yet to be defined. Evidence suggests that glioblastoma (GBM) cells sense and respond to the stiffening of the tumour microenvironment with an increase of its malignant and invasive characteristics. Thus we hypothesize that durotaxis might play a key role in the spreading of tumour cells into the stiffened microenvironment. To directly characterize the impact of local stiffness on directional migration, GBM cells were cultured on a uniform chemical and topographical polydimethylsiloxane (PDMS) substrate displaying a stiffness gradient, imaged and tracked by time-lapse microscopy and tracking software. Preliminary data revealed that different GBM cell lines respond to a stiffness gradient with directed migration to stiffer or softer patterns in a cell type dependant

manner Furthermore, we determined that cytochalasin inhibition was sufficient to inhibit glioblastoma movement but not durotaxis, suggesting that alternative signalling is used to respond to durotactic directional cues. The speed and length of the directional migratory response to stiffness gradients was found to depend on the magnitude of stiffness of the microenvironment encountered by the cell. By isolating external environmental cues and controlling stiffness gradients, we will better understand if a durotactic mechanism has an overall or cancer-specific impact on disease progression.

#161 - Photocatalytic activity of polymer nanoparticles modulates intracellular calcium dynamics and reactive oxygen species in HEK-293 cells

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Light induced modulation of living cells activity is raising more and more interest for its high throughput, selectivity and resolution with respect to currently available techniques. UV radiation is absorbed by proteins and nucleic acids, leading to conformational changes dangerous for cell viability. Near Infrared (NIR) and InfraRed (IR) light are absorbed by water molecules, whose relaxation generates thermal gradients used for pain treatment. Visible light stimuli have been less studied than NIR and IR for the absence of possible absorbers in animal tissues, despite the possibility of achieving a modulation different from the thermal one.

Technologies as photobiomodulation and optogenetics are those involved in the use of visible light. The former provides for the direct illumination of tissues or cells, where visible light is absorbed by specific respiratory-used organelles: mitochondria. Despite being potentially a way to modulate cellular metabolism, no reproducible and reliable experimental protocol has been developed, yet. The latter needs viral transfection of photosensitive proteins to enhance cells sensitivity to light. Since this strongly limits the bed-side, the need of different approaches has to be addressed.

Semiconducting polymeric materials perfectly suit as an alternative for their strong biocompatibility. Moreover, they offer tuneable absorbance and versatile fabrication, being easily synthesized in form of flakes and nanoparticles, making them perfect candidates for on demand drug delivery and targeting of single cells.

We present here promising nanoparticles based entirely on poly(3-hexyl-thiophene) semiconducting polymer, which are able to be internalized within the cell cytosol without the need of stealth strategies or viral transfection. Once internalized, they are photoexcited in the intracellular environment, where oxygen-mediated reactions trigger on demand calcium releases, opening to possible modulation of cellular metabolism and related functions, namely proliferation, differentiation and cell fate.

Delayed cytotoxicity estimation assessed the long-time biocompatibility of the triggered effect, electing these nanoparticles as possible photo-actuators for metabolism control.

#162 - Interaction of Single Cells with Organic Monolayers

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Organic monolayers were used as functional surfaces for investigating morphologically the cell-surface interaction.

Specifically, Pentacene, Sexithiophene and PDI8-CN₂ monolayers were grown on Si/SiO_x by depositing the same amount of molecules in three sequential steps, spaced out by a post-deposition annealing at specific substrate temperatures (50°C for Pentacene, 100°C for Sexithiophene and 80°C PDI8-CN₂) [1]. This method allows growing monolayers with high surface coverage (up to 98%) and *quasi* free of defects, i.e. with less holes and no overhead structures. In the case of Sexithiophene molecules, Scanning Probe Microscopy measurements and computer simulations have shown the growth processes behind of this re-organization process.

These organic monolayers were then employed for investigating the interaction of single cells with morphologically and chemically controlled surfaces. As well known, the cell morphology changes accordingly to the adhering surface [2]. Cell samples were firstly characterized by means of epifluorescence microscopy, in order to prove their biocompatibility *vs* the bare Si/SiO_x. In particular, MCF10A cells adhere and proliferate on organic monolayers (higher cell-surface affinity), while they grew in 3D structures on the bare Si/SiO_x, because the cell-cell interactions is maximized.

Scanning ElectroChemical Microscopy (SECM) imaging were performed on each sample for assessing cells morphologies [3]. The height, the surface contact area, the half-width half-maximum and the inclination angle of the cell were measured from SECM images. In particular, the inclination angle was proposed as an alternative and more correct measurement of the cell-surface interaction despite to the usually adopted contact angle. Such morphological parameters permits to outline a "morphological figure of merit" of cells *vs* surfaces, defining the specific cell-surface interaction.

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#163 - Molecular adsorption on 2D insulators and semiconductors

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The deposition and organization of monolayers, multilayers and heterostructures of organic molecules on hexagonal boron nitride (hBN) and black phosphorus (bP) is studied using ambient atomic force microscopy. It is possible to exploit the two-dimensional nature of extended supramolecular arrays of molecules stabilized by hydrogen bonding to form heterostructures by sequential deposition of one supramolecular layer on another. This can be achieved using both solution deposition and sublimation. These arrays can be used to passivate the surfaces of reactive materials, such as bP, and, also, to modify their optical properties. We also investigate the dependence of the fluorescence peak energy on in-plane spatial ordering of molecules, and, also, on interactions with the substrate. In particular, we find a dependence of the fluorescence energy on the refractive index of the substrate. The bi-component array melamine cyanurate provides a particularly versatile substrate supporting the orientationally-controlled epitaxial growth of terphthalic acid, trimesic acid and several strong fluorophores including perylene and porphyrin derivatives. The energetics controlling the growth of heterostructures has been investigated using molecular dynamics calculations and we find excellent agreement between theory and experiment.

#164 - Characterization of MoS₂ nanosheets grown by CVD methods

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Molybdenum disulphide, MoS₂, consisting of single or few atomic sheets, are known to show unique physical and chemical properties, making them suitable for integration in devices such as field effect transistors, photodetectors and low-power and ultra-scaled (opto-)electronics [1, 2, 3, 4]. However, such properties have been mainly proven starting from the exfoliation of layers from bulk MoS₂, a method which hardly limit the use of MoS₂ nanosheets in practical applications. Among the proposed routes to synthesize MoS₂ nanosheets, chemical vapor deposition (CVD) based approach is gaining consideration because of the good balance between relatively low installation and running costs, and the rich flexibility in terms of process parameters tuning and sample surface sizing and conditioning.

Thanks to the abovementioned characteristics, we grew MoS₂ nanosheets in 2 CVD apparatuses: (i) an home-made system consisting of a single hot wall quartz tube type furnace [5, 6] and (ii) a commercial automated controlled CVD system consisting of 2 coupled/decoupled furnaces. We started from evaporated MoO_x (x=2÷3) thin films or MoO₃ powder on SiO₂/Si substrates and S powder as precursors; in some cases we pre-treated SiO₂/Si substrates with organic molecules, such as PTAS [7], as aid to MoS₂ growth. We also varied the process parameters, such as process temperature, pressure and duration.

We characterized the so-grown MoS₂ sheets with a bunch of techniques to gain knowledge on their physical and chemical properties: Raman spectroscopy, X-ray photoelectron spectroscopy, atomic force microscopy, scanning electron microscopy. By combining the results from the analyses and the growth conditions, we could rationale (and in some cases control) peculiar MoS₂ features, such as the number of MoS₂ sheets, the shape and size of the domains or the degree of granularity, the size/amount of substrate area covered by MoS₂.

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#165 - Application of graphene-based flexible antennas in consumer electronic devices

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We describe the fabrication and characterization of Near-Field Communication (NFC) devices based on highly flexible, carbon-based antennas composed of stacked graphene multilayers. This material features a high value of conductivity (4.20×10^5 S/m) comparable to monocrystalline graphite, but is much more flexible and processable. We first studied the replacement of metal with carbon antennas using computer modelling, to select the best design. Then we manufactured several devices to be used according to the communication protocol ISO/IEC 15693. The inductance of the G-paper antennas was tested before and after hundreds of thousands of bending cycles at bending radii of 45 and 90 mm. During bending the self-resonance frequency and inductance peak showed minimal variation and the resistance at 1 MHz changed from 33.09Ω to 34.18Ω , outperforming standard, commercial metallic antennas. The devices were successfully tested by exchanging data with a smartphone and other commercial NFC readers, matching the performance of standard, commercial metallic antennas. The graphene antennas could be deposited on different standard polymeric substrates or on textiles. Smart cards, flexible NFC tags and wearable NFC bracelets were prepared in this way to be used in electronic keys, business cards and other typical NFC applications.

¹“Application of graphene-based flexible antennas in consumer electronic devices”, A. Scidà et al., *Materials Today* 21, 223, 2018

#166 - Fast detection of water nanopockets underneath wet-transferred graphene

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We report an investigation of the graphene/substrate interface morphology in large-area polycrystalline graphene grown by chemical-vapour deposition and wet-transferred onto Si wafers. We combined spectroscopic ellipsometry, X-ray photoelectron spectroscopy and atomic-force microscopy in order to yield morphological and chemical information about the system. The data showed that wet-transferred samples may randomly exhibit nanosized relief patterns indicative of small water nanopockets trapped between graphene and the underlying substrate. These pockets affect the adhesion of graphene to the substrate, but can be efficiently removed upon a mild annealing in high vacuum. We show that ellipsometry is capable of successfully and reliably detecting, via multilayer dielectric modelling, both the presence of such a spurious intercalation layer and its removal [1]. The fast, broadly applicable and noninvasive character of this technique can therefore promote its application for quickly and reliably assessing the degree of adhesion of graphene transferred onto target substrates, either for ex-post evaluation or in-line process monitoring.

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#167 - Electron tomography of 2D materials in the Scanning Electron Microscope

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The recent approaches to the fabrication of functional materials exploits the peculiar electrical properties of two-dimensional (2D) materials either pure or combined with other nanostructures.

The modeling of 2D hybrid structures calls for an investigation of the spatial disposition of the constituents at the micrometric scale. Scanning electron microscopy could easily cover such an intermediate magnification range; however, a quantitative interpretation of the sample spatial arrangement is beyond the capability of the conventional secondary-electron (SE) imaging.

The scanning-transmission imaging in the SEM (STEM in SEM or T-SEM) is a standard implementation for the SEM platform, suitable for a prompt observation of low-density and 2D materials, and recently demonstrate a technically viable realization of electron tomography in the SEM [1-2]. The acquisition of several STEM projection images at different tilt angle and a Radon-transform-based algorithm, allows one to obtain a three dimensional reconstruction of the specimen.

The tomographic reconstruction algorithm introduces the additional requirement for the detection strategy: the STEM signal is based on the intensity of the electrons forward-scattered by the thin specimen, and the mass-thickness contrast should vary monotonically when the sample is rotated and projected from different directions. A tailored detector for transmitted electrons and a specific imaging strategy has been implemented in the SEM for the purpose of electron tomography in the SEM.

The acquisition of experimental projections and the workflow of tomographic reconstruction has been applied to different test samples, including a graphene-ZnO heterostructure. The comparison between the images obtained with two conventional SE detectors and the one obtained operating the SEM in the transmission imaging mode reveals the enhanced contrast and visibility for the ZnO nanoparticles, which are clearly recognizable from the graphene matrix and the supporting lacey carbon film of the TEM grid. It turns out that the tomogram, obtained by standard retroprojection and followed by iterative refining, retrieves the spatial disposition of the hybrid system with adequate resolution. The proposed approach to electron tomography in SEM is suitable to a quantitative assessment three-dimensional structure of the sample.

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Chemical Functionalization and Characterization of 2D Materials	Matteo Ceppatelli
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Electronic and Photonic Devices for Biological Applications	Michele Muccini
First Principles Modelling of 2D Materials and their Heterostructures	Massimo Rontani

#168 - Sensing energy (heat) exchange at the nano-scale during H₂-uptake on Ti-functionalized graphene

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In the last decades, research has resulted in an increasing number of devices at the micro- or nano-scale. Sensors, catalyzers, and energy storage systems are more and more designed as nano-devices, which represent the building blocks for commercial "macroscopic" objects. A general method for the direct evaluation of the energy balance of such systems is not available at present. Calorimetry is a powerful tool to investigate energy exchange, but it usually requires macroscopic sample quantities (10-100 mg). Here we report on the development of an original experimental setup able to detect temperature variations as low as 10 mK in a sample of ~10 ng using a sensitive gold film thermometer having physical dimensions of 5x5 mm². The technique has been utilized to measure the enthalpy release during the adsorption process of H₂ on a titanium decorated monolayer graphene (Ti-MLG). We chose the Ti-MLG system because of the previous extensive investigations on solid-state graphene-based devices for their application in the hydrogen storage field [1,2,3], which makes it a benchmark and a reference.

The MLG is grown by the CVD method on a copper foil and successively transferred on the thermometer, while the gold surface has been characterized by Scanning Tunnelling Microscopy before and after graphene transfer. Thermometric measurements are performed monitoring the resistance variation of the Au film with temperature. After a careful thermometer characterization and calibration, a thermal signal during hydrogen loading has been detected. The sensitivity of this thermometer allowed to detect a hydrogen uptake of ~10⁻¹⁰ moles, corresponding to ~0.2 ng, with a temperature increase of $\Delta T=0.065$ K and an enthalpy release of ~23 μ J [4]. Each measurement has been cross-checked through Thermal Desorption Spectroscopy, extracting the loaded hydrogen amount and the binding energy from the Redhead equation. Our experimental setup extends the application of calorimetry to nano-scale devices allowing, for the first time, the evaluation of the energy balance on nano-gram samples, very useful for the study of 2D materials. Moreover, this technique allows scalability towards even lower sample dimensions while the energy evaluation is non-destructive because the technique does not require desorption.

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#169 - Investigation of the modulation of the non-covalent interaction between 2D BP and fluorescent pyrene derivatives endowed with different functional substituents

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Owing to its semiconductor nature, phosphorene (bidimensional black phosphorus, 2D BP) is one of the most studied 2D material of the last years. Surface functionalization is a key factor in the development of this 2D semiconductor as an effective material platform to be implemented in real-setting applications. Indeed, several chemical strategies can be adopted in this framework in order to modulate phosphorene band gap [1], to realize active hybrid heterostructures [2] and to protect 2D BP from oxidation [3].

Herein, we perform a throughout photo- and chemical-physical study in order to get insights on the nature of the chemical interactions between 2D BP with organic luminescent conjugated compounds bearing different functionalities. Together with their unsubstituted counterpart, we selected two pyrene derivatives with boron-functionalities such as the pyren boronic acid (PBA) and the pyren boronic ether (PBE), which have been dispersed in 2D BP exfoliated suspension. Specifically, the presence of the boron-functionalities is correlated to the widely-recognized chemical affinity between phosphorus atom (P) with boron atom (B)[4].

As a first output, ³¹P magic-angle spinning NMR spectrum recorded for the first time in a suspension highlighted a non-covalent nature of the interaction between 2D BP and PBA.

Then, DFT calculations were performed in order to discriminate the effectiveness of the different functionalities in mastering the interactions between the 2D BP and the organic conjugated moieties. Indeed, the stabilization energy between phosphorene and PBA is expected to be higher than that of the phosphorene/PBE system. Moreover, the stabilization energy increases when BP is oxidized.

As a final experimental validation, time-resolved lifetime fluorescence spectroscopy revealed that PBA and PBE are energetically stabilized with respect to unsubstituted pyrene given they present almost 5-time-higher emission decay time constants.

Collectively, all these results showed up that (i) the multi-technique and inter-disciplinary experimental approach here presented is suitable assessing the intimate nature of the interaction between 2D BP and active molecules and (ii) the energy-stabilized semiconductor hetero-system comprised by 2D BP and suitably-functionalized pyrene moiety is prone to be used as active layer optoelectronic devices.

Acknowledgments

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#170 - Defect Engineering Of Colloidal Two Dimensional Transition Metal Dichalcogenides Via Atomic Passivation

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Two-dimensional transition metal dichalcogenides (2D-TMDs) with their superior and versatile physical properties are at the forefront of materials innovation holding the promise to fulfill the technology requirements for next-generation semiconductor devices.

Colloidal approach for 2D-TMD material synthesis provide key advantages over other existing methods combining mild synthetic condition, precise control over 2D-TMD composition and structure, to the full value of obtaining a 2D-TMDs ink that can be deposited at low temperatures over large areas in a single and straightforward step by exploiting solution based deposition techniques.

However, the presence of intrinsic defects in colloidal 2D-TMDs, which critically degrade their optoelectronic properties, and the lack of an effective atomic defect passivation scheme tailored for colloidal 2D-TMDs, hinder their extensive use in several optoelectronic platforms.

Here, we report a solution-phase passivation strategy to engineer defect states in colloidal 2D-TMDs leading to a superior control over their energy band structure, while preserving their colloidal stability. In particular, we are able to passivate sulfur vacancies in colloidal WS₂ nanoflakes by exploiting halide ligands, which possess compatible size with sulfur vacancy sites and strong affinity to under-coordinated transition metal atoms, enabling highly effective passivation. We found that halide ligands suppress sub-band states originated from sulfur vacancies mitigating the adverse effect of defects and contributing to increase photoluminescence quantum yield. Furthermore, we examine relaxation processes using photoluminescence excitation (PLE) spectroscopy, time-resolved spectroscopy, and *ab initio* density functional theory (DFT) which support the effectiveness of our approach to engineer band structure of colloidal 2D-TMDs to finally obtain a 2D-TMDs system with reduced sub-band defect states.

#171 - Building materials by assembly of ZrO₆ and R(H)PO₃ blocks: alpha-type layered structures with unusual reactivity

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The chemistry of layered Zr(IV) phosphates and phosphonates has been studied since 1960 [1]. In the last decade the discover of a new synthetic approach paved the way for the development of several functional materials, consisting of a robust inorganic backbone

supporting covalently bonded organic groups. The new synthetic route was developed in 2009 for the preparation of alpha-type nanocrystalline zirconium phosphate (n-ZrP) [2]. According to this procedure, when concentrated phosphoric acid is added to a solution of a zirconyl organic salt in aliphatic alcohols (ethanol propanol, butanol), a semitransparent gel is obtained, consisting of solvent intercalated ZrP packed layers, with an average planar size around 50 nm. The P-OH groups of n-ZrP turned out to be more reactive than those of the corresponding microcrystalline compound and undergo topotactic anion exchange reactions in quite mild conditions, leading to mixed zirconium phosphate phosphonates with general formula $Zr(O_3POH)_x(O_3PR)_{2-x}$ where R is an organic functional group; alkyl, phenyl, aminoalkyl groups were successfully anchored to the layer surface [3a, 3b]. n-ZrP also reacted with mono- and di-alkyl epoxides, providing organic derivatives in which the organic groups are bonded to the inorganic backbone through P-O-C bonds [3c].

The use of the above compounds for the preparation of polymer nanocomposites and in heterogeneous catalysis will be showed.

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#172 - Epitaxial ordering of tetracosane on 2D black phosphorous into air-protecting dielectric multilayers

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Few- and single-layer black phosphorous (2D BP) is among the most promising emerging semiconducting 2D material. 2D BP shares some structural similarities with other 2D materials, but it is generally more reactive than most of them. 2D BP is consequently more prone to degradation in air but also more suited to create atomically-controlled heterostructures for a wide range of applications.[1] Heterostructures based on 2D BP and other inorganic 2D materials have indeed shown a good stability and excellent functionalities.[2] Even epitaxial self-assembled monolayers (SAMs) of organic molecules on 2D BP have shown a good protecting ability, and can be formed more easily via solution.[3]

In this framework, we studied a Van der Waals (VdW) epitaxial system composed of 2D BP coated with tetracosane (a n-alkane with 24 C atoms). High-resolution AFM of a SAM of tetracosane on a bulk BP crystal (used as a model system) showed the co-existence of both disordered and epitaxial domains. MD simulations and high-resolution AFM revealed that tetracosane chains are energetically favored to align along two principal crystalline axis of BP (at +35° and -35° with respect to the armchair direction). This epitaxial arrangement was also observed for tetracosane on exfoliated 2D BP. Here, ordered domains are able to inhibit the oxidation of 2D BP keeping the system unperturbed for around 1h (instead of a few minutes for pristine 2D BP), while amorphous/disordered domains are much less efficient. The protecting properties of the epitaxial domains were improved through a fine tuning of the deposition/processing conditions on the 2D BP flakes: tetracosane ordered multilayers showed a 18-fold enhanced protecting functionality with respect to monolayers.

Electrostatic force microscopy (EFM) was then employed as non-trivial technique to investigate on the functionality of the system, in detail on the electrical polarization of pristine and alkane-coated 2D BP. EFM supported the qualitative conclusion that (i) the oxidation process impacts on the electrical properties of BP, (ii) the multilayered tetracosane offers excellent protection against oxidation and (iii) is able to significantly depress BP polarization. Indeed tetracosane monolayers and multilayers responded to electrostatic stimuli as expected in the case of an electrical insulator. EFM results open to the implementation of the studied VdW epitaxial heterostructures based on 2D BP as stable components and devices with a metal-insulator-semiconductor architecture.[4]

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#173 - Molecular Engineering Approaches to High Performance Materials in Organic Optoelectronics

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π -Conjugated functional organic materials are envisioned as essential components of next-generation optoelectronic devices such as flexible displays, low-cost solar panels, electronic papers, printable RFID tags, and molecular sensors. These new technologies are expected to revolutionize the role of electronics in everyday life and complement current inorganic-based optoelectronic devices that have greatly impacted our society starting from the second half of the 20th century. To this end, the theoretical design and synthetic tailoring of π -conjugated architectures have been very crucial to optimize the physicochemical and optoelectronic properties of organic materials for a particular application. Herein, we demonstrate that thin-films prepared from properly designed organic semiconductors based on BTBT, oligothiophene, and indenofluorene moieties form favorable nanostructures and morphologies, which can be used for a variety of high-performance organic optoelectronic applications.

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#174 - Polar conjugated polymers: eco-friendly materials as new platform for advanced applications

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The development of new materials is pivotal for the exploitation of the new technologies. One important class of emerging semiconducting materials is represented by conjugated polyelectrolytes (CPEs) comprising an electronically delocalized π -conjugated backbone with pendant groups bearing polar or ionic functionalities [1]. CPEs combine the typical properties of polymeric semiconductors, such as chemical tunability, easy processability, lightness and flexibility with the growing demand for environmentally friendly materials. In fact, the incorporation of polar/ionic side groups increases the solubility in water and alcohols, which can potentially provide increased biocompatibility for sensor applications and more environmentally friendly manufacturing options. Moreover, the possibility for orthogonal solvent processability opens the way to all-solution-processed organic multilayer devices.

We have shown that the insertion of a thin film of a properly synthesized CPE between active layer and electrode in organic electronic devices like OLED[2], OPV[3] and recently OLET[4] is crucial for achieving a high-performance device, due to the formation of permanent dipoles. In this view, we have designed, synthesized and tested CPEs combining different monomers in the conjugated backbone as fluorene, thiophene, benzodithiazole and cyclopentadithiophene with pendant polar and/or cationic or anionic groups. The same class of CPEs, thanks to their conjugated backbone and ionic functionality have shown to remarkably enhance the pseudocapacitance of MXene-based hybrid 2D materials [5]. Interfacial engineering has been identified recently as an essential approach for maximizing efficiency and stability of electronic devices. In this contest, the intrinsic hybrid characteristics of CPEs make them promising candidates for tuning the interface properties of inorganic materials too.

Moreover the use of CPE in biological applications seem to be very promising thanks to their high tunability, water solubility and good biocompatibility

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#175 - Biopolymer assisted single-step perovskite growth toward scalable and high efficiency optoelectronic devices

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Hybrid perovskite based materials, thanks to their attractive optoelectronic properties, have revolutionized the field of photovoltaics, showing high power conversion efficiency competing with silicon and thin film technologies [1]. High reproducibility and stability to moisture over operational time via low-cost fabrication technology, and in particular deposition techniques enabling for large area device fabrication are currently object of study towards photovoltaic market demands [2]. Different approaches have been investigated to control perovskite crystalline structure, morphology and moisture stability such as additive inclusion, thermal annealing, use of different kind and molar ratio of precursors [3]. The most widely used deposition method to obtain a high quality perovskite film requires the dripping of a non-solvent in the last stage of spin-coating, that strongly limits the up-scaling. In our work, we develop a simple one-step deposition method (antisolvent free) by using a biopolymer as templating additive to control the perovskite film growth. The MAPbI₃ precursors solution containing the additive is easily deposited by spin coating and allows for a very thick and smooth film without requiring a dripping solvent. The grain size and the morphology of the film are highly influenced by the precursors and additive concentrations. The performance of the as-made biopolymer-perovskite composite as active layer in a solar cell device was explored in a standard inverted architecture, namely ITO/poly-TpD/MAPbI₃-polymer/PCBM/bcp/Al, also compatible with large area processing and potentially flexible devices. The best device showed high PCE up to 17.2% under standard AM1.5 illumination and very high Voc of 1.07 V, highlighting the potential of this simple approach as general method to allow a control the perovskite film formation in a single step.

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#176 - Organic printed transistors using poly (vinyl formal) as gate dielectrics

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Poly (vinyl formal) (PVF) is known for its high insulating property and is widely used as an inexpensive resin in the industry. Recently the use of the PVF in the form of a nanofilm is investigated and a passive electric component was developed. Its electric properties are proven to be almost consistent with the bulk properties. In this work, we report the use of PVF film as a gate insulator in an organic transistor.

On surface-modified glass substrates with poly (methyl methacrylate) (PMMA), we first printed PEDOT:PSS source and drain electrodes with channel length of about 80 μm and width of 1000 μm , then an n-type organic semiconductor of poly{[N,N'-bis(2-octyldecyl)-1,4,5,8-naphthalenedicarboximide-2,6-diyl]-alt-5,5'-(2,2'-bithiophene)} (P(NDI2OD-T2)), Activelink N2200) and a p-type organic semiconductor of poly(3-hexylthiophene-2,5-diyl) (P3HT) using an inkjet printer. Then PVF nanofilms with various thicknesses were transferred. Finally, PEDOT:PSS gate electrodes were printed by inkjet printing. The PEDOT:PSS/PVF (65 nm)/PEDOT:PSS capacitors showed the capacitance of 33 nF/cm² and n-type transistors with the same gate dielectrics operated under 10 V with a mobility of 0.08 cm²/Vs. Due to the high insulating property of PVF, the leakage current was suppressed to less than 10 fA.

To obtain PVF nanofilms, nanofilms are first fabricated on Si buffer then released on water surface, therefore the recollection is mandatory. To transfer the PVF nanofilms on target sample, we demonstrated 3 methods: dry recollection to first recollect PVF film on metal wire and transfer it on target sample, wet recollection to dip the target sample in water and collect the nanofilm, and top-dry recollection to approach the target sample from the top of the floating nanofilm and attach with van der Waals force. All of the transfer protocols showed almost equivalent properties of the transistors afterward. The wide range of the recollection methods enables more variety in the device fabrication and applications.

#177 - High sensitive direct X-ray detectors based on solution-processed cesium-containing triple cation perovskite thin film

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The strong demand for large area high-energy radiation (e.g. X- and γ -rays) detection systems combining high sensitivity and low-cost fabrication, has pushed the research in the last ten years to develop and design both novel materials and device geometries. Organic semiconductors have attracted a great attention¹. However, their low atomic number strongly limits the high-energy radiation absorption

and, blending the organic solution with high Z nanoparticles² is necessary to maximize their radiation absorption. Hybrid organic-inorganic perovskites have been recently proposed as alternative materials for X- and γ -photon direct detection, thanks to their high Z constituent atoms, e.g. Pb in lead-halide perovskite, combined with a high charge mobility. Recently³, the first results on a thin-film direct X-ray detector based on solution-processed methylammonium lead triiodide (MAPbI₃) perovskite, has been reported, with sensitivity values up to 25 $\mu\text{C mGy}^{-1}\text{cm}^{-3}$.

In this work we report on thin film X-ray direct detectors based on solution processed Cesium-containing triple cation perovskite, namely Cs_{0.05}(MA_{0.17}FA_{0.78})Pb(I_{0.8}Br_{0.2})₃ (CsFAMA), where inorganic cesium (Cs) has been added to mixed organic cations (methylammonium (MA) and formamidinium CH₃(NH₂)₂⁺ (FA)) and mixed halides (I and Br). Such a triple cation perovskite formulation has been demonstrated to overcome the thermal and structural instabilities of MA/FA mixture, providing high efficiency perovskite solar cells with stabilized power conversion efficiencies⁴. We demonstrate how direct X-ray detectors based on solution processed CsFAMA thin film possess a high sensitivity, up to 80 $\mu\text{C mGy}^{-1}\text{cm}^{-3}$ in short-circuit conditions, higher than the values reported for MAPbI₃ based detector in similar operating conditions³, and up to 1,000 $\mu\text{C mGy}^{-1}\text{cm}^{-3}$ when operated under small (-0.4V) reverse bias condition. The direct comparison between detectors based on MAPbI₃ or CsFAMA shows that the X-ray sensitivity and $\mu\tau$ product are more than one order of magnitude higher for CsFAMA. The optical properties (transient photoluminescence, absorbance and photoluminescence spectra) show the superior carrier lifetime of CsFAMA, as well as, the PLQE. What is more interesting, CsFAMA present ambipolar charge transport, where both electrons and holes have comparable mobility.

The employment of stable CsFAMA perovskites as direct X-ray detectors pushes the performance of thin-film based ionizing radiation detectors and boosts the vision of solution processed, large-area and flexible direct X-ray detectors operated at low bias and thus suitable for applications like wearable electronics.

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#178 - EFFECT THE ORGANIC COATING EFFECT ON THE MAGNETIC BEHAVIOR OF SMALL COFe₂O₄ NANOPARTICLES

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The electronic, structural, and magnetic properties of nanoparticles are known to be modified at and near the surface. Interestingly, the addition of a non-magnetic surface coating of magnetic nanoparticles affects the surface properties [1]. In our effort to study magnetic nanoparticles in ionic liquids for magnetothermoelectric applications, we study the effect of different ligands bonded at the surface of the nanoparticles on their magnetic behavior.

We study two different organic surfactants: diethylene glycol (DEG) and Oleic Acid, bonded at the surface of CoFe₂O₄ nanoparticles [2]. We perform DFT calculations using the VASP package [3] in order to study the modification of the structure of the CoFe₂O₄ surface in the presence of these two different coatings. The cationic distribution used was the one observed in Mössbauer spectroscopy [2]. Our results show: that (a) different spatial distortions of the surface atoms for the two different coatings, (b) the net moment is found to be larger for the DEG coating and (c) the presence of the organic coating results to the increase of the surface anisotropy that is larger in the case of oleic acid.

DFT results were used as input in a mesoscopic scale model of an assembly of interacting coated CoFe₂O₄ nanoparticles in which each particle is represented by 3-macrospins [4]. We use the Monte Carlo (MC) simulation technique with the implementation of the Metropolis algorithm to calculate the isothermal hysteresis loops and the temperature depended magnetization curves. Our MC results demonstrate that in the case of DEG coating the saturation magnetization and the blocking temperature increases whereas the coercive field decreases compared to the oleic acid surfactant. The MC results are compared and they are in very good agreement with the experimental findings.

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#179 - Ambipolar Vertical Organic Field-Effect Transistors and Inverters.*Elisabetta Zuccatti - CIC nanoGUNE*

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Organic devices aim at opening the path towards a forthcoming generation of low cost, flexible¹ and biocompatible² electronic technology. In particular, and having in mind logic operations, an important goal is to perform Boolean functions through logic gates. In this work we present an inverter built upon ambipolar vertical field-effect transistors (VOFETs). The VOFET have been fabricated on standard Si wafers and using CVD graphene and aluminium as source and drain contacts. In this particular case, diketo pyrrolo-pyrrole derivative (DPP-4T)³ is employed as ambipolar semiconductor. In our devices, the graphene weak electric field screening allows the gate voltage to influence both the charge injection into the semiconductor as well as the charge transport in the organic material^{4,5,6}. Adopting an ambipolar material we achieve both n-type and p-type operations without the need of combining different molecular species, and with a simplified device fabrication process.

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#180 - Plasma deposited nano/bio composite coatings for drug-release and other biomedical applications

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Atmospheric pressure plasma processes are widely used for tailoring the surface properties of biomedical materials, as well as in other applications, e.g., decontamination/sterilization of materials, wound healing and cancer treatments, in the recently born discipline of Plasma Medicine. In certain experimental conditions Aerosol-Assisted Atmospheric Pressure Plasmas (AA-AAP) systems, that can be set in Dielectric Barrier Discharges (DBD) or in Atmospheric Pressure Plasma Jets (APPPJ), can deposit nano/bio-composite coatings on substrates of biomedical interest. This class of thin films is made of biomolecules (peptides, drugs, enzymes, etc.) embedded in an inorganic or organic matrix, from which they can be released in active form in solution or other media for drug-release, anti-bacterial, cell-growth, sensing and other applications of potential use in Medicine. When certain experimental approaches are used, such coatings can be synthesized as free-standing "NanoFilms". This talk will show examples of Plasma Deposition techniques in biomedical and other applications, with focus on the deposition and characterization of nano/bio-composite coatings embedding and releasing active lysozyme, vancomycin, gentamicin and other species in water media.

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#181 - Nanoengineering cyclodextrin and photosensitisers for targeted PDT and imaging

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Cyclodextrins (CDs) offers, either as molecule or in self-assembled form, functional constructs to bind PS guests by non-covalent interactions. In the recent past, we reported the design of different supramolecular assemblies of amphiphilic CDs with high efficacy for application in PDT and aPDT [1]. Actually, the design of novel nanophototherapeutics for PDT generally complies with efficient uptake of PS within tissues, cell membranes and/or intracellular components with production and diffusion of singlet oxygen in the neighboring areas to the sites of action. Here we report a brief overview on the most recent outcomes on nanoparticles (NPs) based on self assembly of CD building block complexing different PSs of undoubted interest for PDT such as Zn(II)-phthalocyanine, Bodipy and Pheophorbide A [2-3]. The choice of CD molecule and eventually the targeting group on it, can determine the amount of entrapped PS within of NPs, modulating the *in vitro* PDT activity, thus allowing spatial-temporal control of PS release *in vivo* applications.

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#182 - A deep insight into the intracellular fate of colloidal semiconductor nanocrystals in vivo

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Due to their tunable and efficient photoluminescence in the UV/VIS range, Quantum Dots (QDs) are promising fluorescent probes for theranostic and FRET-based biosensing *in vivo*. InP QDs recently emerged as the best candidates for biomedical applications, being less toxic and more stable than CdSe QDs, considered in a first time. Therefore, prior to any application, the biocompatibility and the stability of InP QDs *in vivo* must be thoroughly assessed.

We tackled this problem by tracking the biodistribution and transformations of two InP QDs formulations, InPZnS core and InPZnS/ZnS/ZnSe core-shell QD, in a model animal system, *hydra vulgaris*. The animals were exposed to sub-lethal doses of QDs that do not alter morphology nor reproduction; nevertheless, modifications of gene expression was observed. Although the optical properties of QDs were lost already after 3h in the animal, synchrotron micro-beam X-ray Fluorescence (μ XRF) imaging detected the presence of Indium in several compartments of *hydra* transversal sections. Micro-beam X-ray Absorption Spectroscopy (μ XAS) revealed no InP species after 3h *in vivo*, but rather oxidized In species indicative of a degradation of the core. This shows that the unexpectedly quick loss of optical properties is not due to clearance but to the accumulation of optically-inactive In species in the animal. Surprisingly, *in vitro* assays showed no degradation of the core, even after 24h at pH 4.5. This highlights the importance of *in vivo* models to assess the biotransformations of nanotechnologies. All synchrotron analysis were carried out on the beamline ID21 of the ESRF, on sections of the animals in the frozen hydrated state, in order to preserve the ionic content and elemental speciation. Our work demonstrates that *hydra vulgaris* is an ideal model to assess the stability of nanomaterials *in vivo*, yet reducing vertebrate experimentation. Synchrotron μ XRF imaging and μ XAS proved to provide unique information about the fate of photoluminescent nanotechnologies after the loss of their optical properties.

#183 - Focus on Bone Cancer Model Via Biomimetic Materials

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Worldwide cancer remains the second-most common cause of death, despite the advances in prevention, early detection, treatment and Osteosarcoma (OS) is the most common type of bone cancer, especially in children and young adults¹.

In the last decades, has been demonstrated the central roles of cancer stem cells (CSCs) in tumour recurrence, metastases and chemo resistance via self-renewal and differentiation; moreover, the interaction with extracellular matrix (ECM) appeared to be fundamental for CSCs signalling pathways². For that reasons, 3D cell culture models are gaining more and more significance for the study of cancer biology because these models are recapitulating the *in vivo* situation of cells much better than the standard monolayer cultures. In the present study, we proposed a more complex *in vitro* 3D model mimicking the *in vivo* tumour microenvironment, with particular focus on osteosarcoma stem cells niche; CSCs and cancer cells were cultured in tradition 2D system and on a natural-inspired hydroxyapatite based scaffolds in order to obtain a 3D cancers stem cells model. CSCs were obtained starting from MG63 and SAOS2 cells line by sarcosphere formation assay³, and long term culture were assess in static and dynamic condition.

The 3D CSCs model were characterised by assessing the proliferative and apoptotic state, the expression of osteosarcoma cancer cells related markers (Oct4, NANOG, SOX2, etc) and by evaluating the interaction of CSCs with biomaterial that guiding the plethora of signalling pathways involved in cancer developing.

In contrast to traditional 2D culturing systems, 3D cultures create an environment that enables cells to contact and interact in all dimensions with the scaffold and other cells in culture.

The exiting results leads to the conclusion that 3D CSCs models resulting in a great advancement for preclinical *in vitro* study, including new drug screening in OS, with the ultimate goal to be applied in personalized medicine.

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#184 - Halloysite clay nanotubes: nano-bazookas for drug delivery

Stefano Leporatti - CNR Nanotec-Istituto di Nanotecnologia

Halloysite nanotubes are cheap, abundant in their deposits, natural green clays with cylindrical structure having a chemical composition similar to that of kaolin. Because of their lumens, high aspect length–diameter ratio and low hydroxyl density on their surface they are readily suitable for a number of interesting applications. In this poster we focus only on their use as ‘nano-bazooka’ drug carriers, able to shoot their cargo against major diseases. Their structure, controlled release and loading are described. We emphasize especially their possible use as novel drug delivery systems with applications in nanomedicine

#185 - Mesoporous silicon-coated microparticles towards biomedical applications

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Porous silicon (pSi) microparticles can be easily obtained by anodization etching of crystalline silicon wafer in HF solution. This is followed by a sonication step in a thermal bath and a surface carboxyl-functionalization process, which leads to light emitting mesoporous microparticles, optically stable for years in ethanol. Furthermore, this sponge-like material is biodegradable, biocompatible, inert and therefore promising for biomedical applications. In particular, the porosity and the photoluminescence make the pSi microparticles suitable for both drug delivery and bioimaging applications.

One of the problems to exploit this material in the biomedical field is the microparticles degradation and the fast quenching of the optical properties in aqueous media (i.e. phosphate buffered saline – PBS). To overcome this problem, we investigated two types of coating: organic and inorganic.

We previously covered the pSi microparticles with covalently attached organic polymers, such as PEG and chitosan, leading to negatively and positively charged surface, respectively, and stabilized their optical properties for several months. First, we evaluated that they were not cytotoxic, by incubating human dendritic cells (DCs) with different concentration of pSi microparticles, up to 100 µg/mL. Then, we proved that they were not activator of the immune response system by ELISA assays, by monitoring the release of immunomodulatory cytokines (IL-6, IL-12 and TNF- α). Furthermore, we obtained good preliminary results in drug loading and release tests, using Cbi (cobinamide) as drug test molecule, with a slow drug release, particularly for PEG-coated microparticles.

But the dimension of the organic polymers caused an increase of the particles size and a reduction of their pore volume, limiting the drug loading capacity. So, we chose another coating approach, by depositing a titanium dioxide layer by ALD (atomic layer deposition) on the mesoporous surface, which allows a thinner, uniform coating with tuneable thickness. We optimized the deposition parameters stabilizing the optical properties for more than six months in PBS.

pSi-TiO₂ microparticles were internalized by the human DCs and maintained their photoluminescence, as it was confirmed by two photon microscopy, and no cytotoxicity was observed. Concerning the immune response, we did not observe any activation after incubating the DCs with pSi-TiO₂ microparticles, but more attention has to be paid in case of co-stimulation with LPS, lipopolysaccharide, leading to an immune response activation.

These promising results of PL stability and compatibility with human DCs open the way for future developments to produce a complete platform for biomedical applications.

#186 - Study of neuronal guidance dynamics in neurodevelopmental disorders models by nano-engineered platforms

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In the brain, cells are exposed to both physical and chemical extracellular stimuli determined by the micro/nano-environment within which they exist: these extracellular instructions orchestrate the wiring of the central nervous system. Although the dynamics of neuronal extracellular sensing is emerging as crucial for neuronal connectivity and functionality, little is known about these processes in pathological conditions (e.g. neurodevelopmental disorders). Nano-engineered substrates are emerging as tools for investigating and tailoring the processes that regulate neuronal extracellular sensing. Nano-structured substrates, for example nano-microgratings (GRs), are in fact able to induce specific topographical stimuli to neuronal cells, resembling *in vitro* several features of extracellular matrix (ECM) cues, and consequently to tune neuronal polarity and migration.

We here developed and demonstrated nano-engineered platforms to study neuronal sensing and migration processes in neurodevelopmental disorders. As pathological models, we focused on the unbalanced levels of ubiquitin ligase E3a (UBE3A), which leads to several neurodevelopmental disorders, such as Angelman Syndrome (AS) and 15-duplication autisms (15dup). By exploiting

electron beam, nanoimprint and/or replica molding, we engineered thermoplastic (in Cyclic Olefin Copolymer) and elastomeric (in PolyDiMethylSiloxane-PDMS) substrates patterned with GRs (i.e. alternating lines of ridges and grooves) having line-widths between 500 nm and 10 μ m. We developed both physical and biochemical (i.e. made of ECM proteins) directional GRs patterns. Here we tested primary healthy-control, AS and 15dup neurons on nano-engineered chips by applying specific biomimetic environmental physico-biochemical stimuli to them and we found guidance deficits in AS neurons.

We propose nano-engineered platforms as advanced devices for investigating neuronal guidance/migration dynamics *in vitro*, as in an enriched environment able to resemble closely the *in vivo* conditions. This work is supported by MSCA-IF-2017 grant Neuroguide (795948).

#187 - Biosurfactant for solubilization and skin permeation enhancement of hydrocortisone

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One of the most widely used approaches for improving drug permeation across the stratum corneum barrier of the skin is the use of penetration enhancers, such as surfactants [1]. Biosurfactants are amphiphilic compounds, produced by microorganisms on their cell surface or secreted extracellularly and exhibit pronounced surface and emulsifying activities [2]. As reported in Abruzzo et al., 2018 [3], a biosurfactant (BC9-Bs), produced by *Lactobacillus gasseri* BC9 isolated from healthy premenopausal women, showed high surface activity together with a low critical micelle concentration (CMC).

The aim of this study was to evaluate the use of BC9-Bs as possible pharmaceutical excipient for skin permeation enhancement of hydrocortisone (HC), a naturally occurring corticosteroid that possess strong anti-inflammatory properties. First, cytotoxic activity of BC9-Bs was assessed on human and murine fibroblasts. BC9-Bs ability to form nanometric self-assembling aggregates at concentration higher than CMC was studied by Dynamic Light Scattering. Moreover, the effect of biosurfactant on HC solubility was investigated. Finally, *in-vitro* permeation studies were performed in order to evaluate BC9-Bs capacity to promote drug diffusion through different membranes, e.g. acetate cellulose, biomimetic artificial barrier Permeapad™, and porcine full-thickness skin. Results showed that BC9-Bs was not cytotoxic and can provide the formation of nanometric aggregates in the range of 180-200 nm. Interestingly, HC solubility and permeability were increased in the presence of BC9-Bs, as a consequence of the drug-Bs interactions.

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#188 - Coexistence of metallic edge states and antiferromagnetic ordering in correlated topological insulators*Giorgio Sangiovanni (I) - University of Wuerzburg*

In this talk I discuss the fate of the helical edge states in quantum spin Hall insulators when the whole system is exposed to strong Coulomb interactions. Using dynamical mean-field theory, I show that the dispersion relation of the edge states is strongly affected by Coulomb interactions [1-2]. In fact, the formerly gapless edge modes become gapped at a critical interaction strength, which is significantly smaller at the edge than its counterpart in the bulk. Thus, the bulk remains in a topologically nontrivial state at intermediate interaction strengths where the edge states are already gapped out. This peculiar scenario leads to the reconstruction of gapless helical states at the new boundary between the topological bulk and the trivial (Mott insulating) edge. Further increasing the interaction strength triggers the progressive localization on the new boundary, the shrinking of the quantum spin Hall region, and the migration of the helical edge states towards the center of the system. The edge state reconstruction process is eventually interrupted by the Mott localization of the whole sample [2]. In the second part I am going to focus on our latest developments regarding the breaking of time-reversal in the antiferromagnetically long-range ordered phase. The resulting non-uniform magnetization leads to the coexistence of spin-ordered and topologically non-trivial states [3].

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#189 - Quantum materials platforms for topological superconductivity and superconducting spintronics*Mario Cuoco (I) - CNR-SPIN*

This talk will deal with effects, phenomena, and quantum materials platforms with great impact in the area of topological superconductivity [1] and superconducting spintronics [2]. Here, the key physical ingredients are spin-orbit coupling, magnetism, superconductivity and topological effects. The generation, manipulation and control of spin quantum states represent core steps for any type of quantum processing. In this context, recently, we have theoretically and experimentally considered the interplay between geometric nanostructuring [3] on the electronic properties and the topological properties of the quantum states in low-dimensional nanomaterials. The basic concepts and phenomena due to geometric effects in low dimensional nanostructures are presented as, for instance, novel metal-insulator transition, generation of topological states of matter [4], topological pumping protocol in an entirely novel solid-state design [5]. Then, I will present the basic twist between spin texture, spin transport and topological pairing in semiconducting-superconducting nanostructures [6,7].

Single spins [8] and Majorana bound states [9] are among the most prospective carriers of qubits, the fundamental units in quantum information science. Starting from these considerations, in analogy with the spin for the spintronics, it is relevant to consider the spin of the Copper pair as a functional element. In this framework, I will discuss the way how spin-triplet pairing is modified at the interface with magnetic systems and consider the interplay of superconductivity and magnetism in heterostructures with a special focus on topological superconductors [10-14].

A short outlook on the materials to be employed for designing and manipulating topological superconductivity will be also presented.

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#190 - Crystallization of Levitons in the fractional quantum Hall regime

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The emergence of self-organized regular patterns in optical solitons has been recently subject of intense investigation, as they promise to be exceptionally useful in quantum communication [1]. In the framework of electron quantum optics, a train of Lorentzian voltage pulses emerges as the solid state counter-part of optical solitons, namely robust ballistically propagating wave-packets carrying an integer number q of electrons called Levitons [2,3]. Using a periodic train of Levitons, we investigate the charge density backscattered off a quantum point contact in the fractional quantum Hall regime, finding a self-organized and regular pattern of peaks and valleys[4]. We demonstrate that the predicted features manifest themselves as unexpected additional dips in the well-studied Hong-Ou-Mandel noise.

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#191 - Exploiting quantum phenomena to design electron transport in nanojunctions

Mario Italo Trioni - ISTM-CNR

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The miniaturization of electronic devices requires a novel approach in the design of such apparatuses. Indeed, as their size scales down towards the atomistic level, their electronic transport properties cannot be rationalized in terms of classical physics, and the use of quantum mechanics becomes mandatory. In this talk we will show that the choice of a quantum approach paves the way towards the conception of a new class of nanojunctions in the emerging field of nano-electronics and spintronics [1].

In this work we shortly illustrate two test cases recently investigated in our group: a) a two-dimensional device made of 3d metal atoms adsorbed on graphene sandwiched between graphene leads. The regular adsorption of Ti, Co, and Fe atoms allows for the filtering of electrons of one spin component only, to a different extent. b) A molecular junction in which a molecule of Fe-porphyrine is contacted between two semi-infinite graphene sheets. Since electrons are forced to flow through the molecule, the intensity of the electric current and its spin polarization are strongly influenced by the structure and the chemical properties of the molecule.

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#192 - Dynamics of electrons in single- and multi-channel Mach-Zender interferometers based on Hall edge states

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Topologically protected edge states in the quantum Hall regime proved to sustain long-distance coherent carrier transport [1]. These chiral and adiabatic conducting channels are able, in principle, to encode and process quantum information via electron quantum optics devices. The realization of such semiconductor quantum logic gates requires to engineer a suitable electrostatic potential profile for the dynamical control of the flying qubits, which is the target of the present research.

We model, with both time-dependent and stationary-state approaches, a multichannel Mach-Zender interferometer with bulk filling factors $n=2$ and $n=1$, where the qubit state is encoded by the Landau level of the propagating carriers or by the channel occupancy, respectively. The potential profile reproduces a modulation-doped 2D quantum well device with smooth barriers and split gates.

In the case $n=2$, a single electron is initialized in the first Landau level and sent to a beam splitter, properly designed to produce a 0.5 coherent mixing of the two Landau levels. The two channels are then split at a mesa [2], whose area induces a phase difference between the beams. The two states are finally recollected on a second beam splitter, where they interfere. The scattering problem for non-interacting delocalized edge channels is initially solved to extract the energy-dependent transmission coefficients and to expand the core system including leads, temperature or bias effects. We then study the dynamical properties of the device describing the traveling charge as a strongly localized Gaussian wave packet of edge states [3].

In the case $n=1$ [4] we address the effect of carrier localization on the transmission properties of the beam splitter (namely, a quantum point contact in the 2DEG), and the effect of electron-electron interaction on the entanglement created between two carriers.

Finally, we will describe the specific parallel implementation of the split-step Fourier method developed to compute the time evolution of the one- and two-electron state.

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#193 - Anomalous behavior of Nb₃Sn local atomic structure revealed by XAFS and RMC models

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Anomalous behavior of Nb₃Sn local atomic structure revealed by XAFS and RMC models.

The exceptional requirements envisaged for the fusion reactors (ITER) and newly conceived large hadron colliders (CERN LHC Luminosity Upgrade) involve cutting edge technology/research developments. Particular attention is devoted to bring the hardest superconductors such as Nb₃Sn, to their maximum performances, such as T_c and critical current. In these extremely demanding contexts, the degradation of T_c induced by strain represents a very critical issue whose understanding requires an accurate knowledge about the relationship between atomic structure, electronic transport and environmental parameters (temperature and pressure), stimulating new researches in this allegedly well known compound [1-3].

Recently synchrotron radiation XRD experiments have detected an anomalous behavior in the P-V (around 5–10 GPa)[4] and V-T (around 200K)[5] curves suggesting the occurrence of structural anomalies likely related to the anisotropy of the directional elastic properties of Nb₃Sn as a function of pressure or temperature. The extended x-ray absorption fine structure (EXAFS) spectroscopy, being a chemical selective local structure probe, provides deeper insight about the nature of these anomalies from a local perspective. Here we present results of Nb K-edge EXAFS measurements as a function of temperature (in the 10 K-300 K range) and hydrostatic pressure (up to 26 GPa)[6]. The EXAFS data analysis has been carried out either applying conventional multi-shell analysis and via Reverse Monte Carlo method [7] in order to directly reveal the distributions of distances, bonding angles and many-body distribution functions. The EXAFS results depict a peculiar trend of Nb-Nb nearest neighbor distances that progressively assume a bimodal shape raising the applied pressure above 5-9 GPa. Inspection of RMC atomic models suggests a dimerization of Nb-chains likely representing the local structure counterpart of the crystallographic anomaly observed in the P-V curves[4-6]. These findings provide novel insight that must be considered in order to improve the knowledge about the structure and electronic transport in these important superconductors.

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#194 - Metal Assisted Chemical Etching of Silicon: a new enabling technology of micro- and nano-fabrication*Lucia Romano (I) - ETH Zürich and PSI*

Metal-assisted chemical etching (MacEtch) of silicon has recently emerged as a new wet etching technique capable of fabricating high aspect ratio nano- and micro-structures of several shapes: nanoporous film, nanowires, 3D objects, trenches, vias, X-ray optics. I will review the fundamentals about the MacEtch mechanism since its discovery in 2000 (Li et al., APL 77 (2000) 2572) and its main applications.

Relevant issues of etching non-uniformity and control of the verticality raise up for high aspect ratio dense patterns. Such challenges have been related to the catalyst instability during long etching processes. I determined the critical role of catalyst and I demonstrated an improved mechanical stability by nanostructuring a thin metal layer through a self-assembly mechanism of de-wetting on top of oxygen-terminated silicon surface (Romano et al., RSC Advances 6 (2016) 16025). Moreover, I will show the implementation of MacEtch technique in a vapor phase to realize high aspect ratio nanostructures. Since it is a “dry” process, it can be used for stiction sensitive applications without requiring supercritical drying steps. Aspect ratio of 1000:1 was scored in few hours, making Vapor-MacEtch a disruptive etching technology that overcomes the nanoscale limits of other gas phase etching techniques such as reactive ion etching.

In particular, I will report on the use of MacEtch as an alternative fabrication method for X-ray diffraction gratings with pitch in the micrometerrange and high aspect ratio. X-ray Grating Interferometry (XGI) imaging is a very promising (Weitkamp et al., Opt. Express 13 (2005) 6296), fast growing and competitive technique for medical, material science and security applications. There is the need to fabricate gratings with i) very high aspect ratio (>20:1); ii) large area (mammography, e.g., asks for a field of view of 20 cm x 20 cm) and iii) good uniformity (no distortions and changes in the duty cycle and depth over the full grating area). LIGA (KIT-Microworks) and reactive ion etching (PSI) microfabrication are conventionally used for creating the grating template in polymer or silicon, respectively. The subsequent Au electroplating forms the absorbing X-ray grating, which is the key component of XGI.

With no limitation on large-area and low-cost processing, MacEtch can open up new opportunities for X-ray optics components and many other applications where high precision nano- and micro-fabrication is required.

#195 - Design, characterization and lithographic application of Si nanocrystals patterns via templated dewetting*Monica Bollani (I) - IFN - CNR*

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Silicon-based nanocrystals represent a promising resource both for next generation electronic devices and for nano-photonics applications but require precise size, shape and position control[1,2]. However owing to their large surface-area-to-volume ratio, thin semiconductor solid films are often unstable upon annealing. Under the action of surface diffusion the film breaks eventually forming isolated islands. This is one of the main factors impeding the use of ultra-thin silicon films on insulators (UT-SOI) for the further miniaturization of electronic components. Here, with an e-beam lithographic method, we demonstrate the ultimate control of UT-SOI dewetting for the precise formation of complex nano-architectures featuring extremely reduced fluctuations of size, shape and positioning (a few %) over hundreds of repetitions and on large scales. The solid state dewetting initiated at the edges of the patterns controllably creates the ordering of nanocrystals (NCs) with ad hoc placement and periodicity [3,4]. The NC size is tuned by varying the nominal thickness of the film while their position results from the association of film retraction from the edges of the lay out and Rayleighlike instability. Islands formation, organization, positioning and composition are studied by dark-field, atomic force and transmission electron microscopy (Figure 1 and 2). Predictive phase-field simulations of the mass transport mechanism, assess the dominant role of surface diffusion providing a tool for further engineering this hybrid topdown/ bottom-up self-assembly method. Finally, we show its potential by fabricating nano-transfer molding for nanoimprinting lithography of titania and silica xerogels on silicon and glass substrates.

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#196 - Synthesis and characterization of novel lead free multiferroic structures*Carmen Galassi - CNR - ISTECE*

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Synthesis and characterization of novel lead free multiferroic structures

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Hybrid ferromagnetic/piezoelectric nanoparticles and ceramics have potential for a wide range of applications due to their tunability, electronic and magnetic properties. Core-shell-type nanostructures of composition BNT-BT0.08 /CoFe₂O₄ (CF), where BNT-BT0.08 is the abbreviation of bismuth, sodium titanate (Bi_{0.5}Na_{0.5}TiO₃, BNT) doped with 8 mol% barium titanate (BaTiO₃, BT) were prepared with different molar ratio of the two phases using the sol-gel synthesis technique. Scanning and transmission electron microscopy confirmed formation of a core-shell structure. XRD pattern of core-shell composites powder reveals only cubic CoFe₂O₄ and rhombohedral Bi_{0.5}Na_{0.5}TiO₃ phases. The densification of the materials is a critical step as the ideal microstructure is nanosized CF grains well dispersed in a BNBT micrometric grains, fully dense matrix. The results of microstructure, dielectric, piezoelectric and magnetic investigations demonstrated that this heterostructures show simultaneously electrical and magnetic behavior, at room temperature.

#197 - Interfaces characterization in the recessed-gate channel of hybrid GaN MISHEMTs

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Gallium nitride (GaN) is an excellent semiconductor for high-frequency and high-power electronics applications. High electron mobility transistors (HEMTs) in GaN are normally-ON devices, due to the presence of the two dimensional electron gas (2DEG) in AlGaN/GaN heterostructures. However, power electronics applications typically require normally-OFF devices, to guarantee fail-safe operation and gate drivers simplicity [1]. Hence, significant efforts have been devoted in the last decade to develop physical methods to control the electrons flow in the channel. The use of a p-GaN gate is currently the only commercial solution for normally-OFF GaN HEMTs [2].

Another promising approach consists in the complete removal of the AlGaN barrier under the gate [3-4], creating a metal insulator semiconductor (MIS) recessed-gate hybrid HEMT (MISHEMT). The recessed-gate hybrid MISHEMT enables to have a positive threshold voltage V_{th} of the MIS channel, preserving a low on resistance R_{ON} in the access regions. Obviously, the most important part of this device is the recessed channel, in which the carriers mobility is influenced by several factors (roughness of the etched surface, defects, quality of the gate insulator, etc). Hence, characterizing the properties of insulator/GaN interfaces and understanding the mechanisms limiting the mobility are key aspects for the progress of the recessed-gate MISHEMTs technology.

In this talk, the properties of recessed-gate hybrid GaN MISHEMTs are discussed, focusing on two cases study of transistors using SiO₂ and AlN/SiN as insulating materials. AlGaN/GaN heterostructures grown on Si substrates were used to fabricate recessed-gate hybrid MISHEMTs. The properties of the recessed gate region were characterized either by means of standard I-V and C-V analyses, as well as using Scanning Probe Microscopy (SPM) techniques (e.g., AFM, C-AFM) [5-6]. In particular, the temperature dependence of the mobility suggested that the main mechanisms limiting the channel mobility are Coulomb and phonon scattering. Hence, the optimization of the interface (reduction of the roughness and of the interface traps) is the route to improve the device behaviour, both in terms of R_{ON} minimization and V_{th} stability. The charge trapping effects of the devices under bias stress have been also discussed.

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#198 - Near Interface Oxide traps probed by transient capacitance measurements on lateral SiO₂/4H-SiC MOSFETs

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In order to overcome the present limitations of silicon devices in terms of power consumption, next generation of power switches will employ 4H-SiC metal oxide semiconductor field effect transistors (MOSFETs) [1]. However, there are still some reliability concerns under discussion within the SiC community. In particular, significant efforts are focused on the comprehension of the phenomena

ruling the stability of the threshold voltage in 4H-SiC MOSFETs [2,3]. In this context, we have recently shown an anomalous temperature dependence of the gate current in lateral MOSFETs, which was described by a modified Fowler Nordheim (FN) tunneling to take into account the changes of the oxide electric field during holes injection [4]. However, the nature and the position of the NIOTs with respect to the SiO₂/SiC interface has not been discussed.

In the present work, this aspect has been considered by carrying out transient capacitance (*C-t*) measurements and state of the art scanning transmission electron microscopy in electron energy loss spectroscopy (STEM-EELS) with sub-nm resolution. The *C-t* measurements as a function of temperature indicated that the effective NIOTs discharge time is temperature independent and electrons from NIOTs are emitted toward the semiconductor via-tunnelling. The NIOTs discharge time was modelled also taking into account the interface state density in a tunnelling relaxation model and it allowed us to locate traps within a tunnelling distance of up to 1.3 nm from the SiO₂/4H-SiC interface [5]. On the other hand, sub-nm resolution STEM-EELS revealed the presence of a non-abrupt (NA) SiO₂/4H-SiC interface. The NA interface shows the re-arrangement of the carbon atoms in a sub-stoichiometric SiO_x matrix. A mixed sp²/sp³ carbon hybridization in the NA interface region suggests that the interfacial carbon atoms have lost their tetrahedral SiC coordination.

These results are particularly useful to understand the physics of the NIOTs and predict their role in the threshold voltage instabilities issue in 4H-SiC power MOSFETs.

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#199 - OLED processing on steel foils, a challenging task for more robust, efficient and sustainable lighting devices*Benoit Racine (1) - CEA**Other Authors: E. Quesnel, T. Maindron, A. Suhm, M. Provost, S. Gétin, J. Micout, B. Aventurier, A. Suhm, F. Sermet (CEA, MINATEC Campus, 17 rue des Martyrs, F-38054 Grenoble cedex, France)*

The production of conformable organic light-emitting-diodes (OLED) requires innovative technologies to meet the market requirements towards more durable, sustainable and performing devices. We present here some of the research developments implemented into the H2020 European LEO project for the achievement of conformable lighting sources on metal foil substrate that may compete with more conventional OLED on plastic technology. The configuration is in Top emission due to the non transmissive metal foil substrate. Among them, a particular attention was paid to the implementation of high reflective anode and high transmissive cathode. The main key issue to be solved was to find a way to make the metal substrate compatible with OLED technology. Moreover, to compensate for the top-emitting OLED configuration imposed by the metal substrate, solutions to generate more light and enhance light extraction have been explored and successfully applied to OLEDs. Silver anode was used to reflect more light and dielectric/metal/dielectric (DMD) multilayer thin films were implemented to increase light output: advantages and drawbacks of this solution will be discussed. Implementation of both shown a significant improvement of the OLED efficiency. Finally an innovative encapsulation was developed to keep bending of the substrate possible while ensuring both mechanical and moisture protection as well as some device conformability.

#200 - Interface Engineering to Enhance the Efficiency of Organic Light-Emitting Transistors*Mario Prosa - CNR - ISMN**Other Authors: Mario Prosa (1), Emilia Benvenuti (1), Mariacecilia Pasini (2), Umberto Giovanella (2), Margherita Bolognesi (1), Francesco Galeotti (2), Michele Muccini (1), Stefano Toffanin (1) (1) Istituto per lo Studio dei Materiali Nanostrutturati (ISMN), Consiglio Nazionale delle Ricerche (CNR), Via P. Gobetti 101, 40129 Bologna, Italy. (2) Istituto per lo Studio delle Macromolecole (ISMac), Consiglio Nazionale delle Ricerche (CNR), Via Bassini 15, 20133 Milano, Italy.*

Organic light-emitting transistors (OLETs) show, in a single device, the fascinating combination of electrical switching characteristics and light generation capability. However, to ensure an effective device operation, efficient injection of charges at the electrodes is required. In this talk, the role that interfacial engineering plays on the figures-of-merits of OLETs is discussed, with particular attention to the use of multifunctional electrodes.

The introduction of solution-processed conjugated polyelectrolytes (CPEs) films at the emissive layer/electrodes interface represents a widespread method to improve the electron injection efficacy and favour the photon-generation process in *p*-type OLETs. Despite the enhancement of performance of the resulting devices is demonstrated, the presence of ionic species in CPEs layers is known to cause complications in the device response due to charge trapping and electric field screening effects. As alternative strategy, the use of conjugated polar polymers (CPPs) is here demonstrated as a new and efficient option to CPEs. [1] Indeed, the conjugated backbones of CPPs are modified with polar non-ionic side groups, thus avoiding ion-depending drawbacks. In this regard, by introducing a layer of polyfluorene containing phosphonate groups (PF-EP) underneath the metal electrodes, a clear improvement of the electron injection properties resulted in a more than twofold increased light-emission (optical power) and a five-times enhanced External Quantum Efficiency (EQE) in *p*-type OLETs, with superior performance in comparison with the relative CPE-containing devices. The great benefit of using a transparent glass as OLET substrate allowed for a deep investigation of the morphological and photoluminescent characteristics of both CPE- and CPP-buried interlayers within complete multilayered OLETs. This, in combination with a detailed investigation of the surface properties, such as morphology, roughness, polarity, allowed to disclose the operation mechanisms of the investigated interlayers and the benefit of using CPPs over CPEs.

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#201 - Replacing PEDOT:PSS HILs with MoS₂ nanosheet HILs in Solution-Processed Light-Emitting Diodes (LEDs)*Umberto Giovanella - ISMAC-CNR**Other Authors: Christian Martella (CNR-IMM, unit of Agrate Brianza, via C. Olivetti 2, 20864 Agrate Brianza (MB), Italy; CNR-ISC, U.O.S. Sapienza, I-00185 Roma, Italy), Francesco Carulli (CNR-ISMAC, via A. Corti 12, 20133, Milano, Italy; Dipartimento di Scienza dei Materiali, Università degli Studi di Milano-Bicocca, via Cozzi 55, I-20125 Milano, Italy), Guido Scavia (CNR-ISMAC, via A. Corti 12, 20133, Milano, Italy), Alessio Lamperti (CNR-IMM, unit of Agrate Brianza, via C. Olivetti 2, 20864 Agrate Brianza (MB), Italy), Benoit Dubertret (Laboratoire de Physique et d'Etude des Matériaux, ESPCI-ParisTech, PSL Research University, Sorbonne Université UPMC, Université Paris 06, CNRS, 10 rue Vauquelin, 75005 Paris, France), Sergio Brovelli (Dipartimento di Scienza dei Materiali, Università degli Studi di Milano-Bicocca, via Cozzi 55, I-20125 Milano, Italy), Alessandro Molle (CNR-IMM, unit of Agrate Brianza, via C. Olivetti 2, 20864 Agrate Brianza (MB), Italy)*

Colloidal nanoplatelets (NPLs), owing to their efficient and narrowband luminescence, are considered as promising candidates for solution-processable LEDs with ultrahigh colour purity. The presence of organic interfacial layers as charge regulators is mandatory

to achieve high NPL-LED performance [1]. However, organic compounds can degrade, thus affecting the operational stability of devices. The characterization in air atmosphere is a simple way to test the stability of LEDs. Degradation of solution-processed LEDs is indeed typically observed below one hour of operation likely due to trapping of oxygen or solvent molecules inside the layers during deposition of the multilayer device architecture. The degradation process is further accelerated by the intrinsic acidity of PEDOT:PSS that is widely used in organic or hybrid devices as hole injecting layer (HIL). The search of alternatives to PEDOT:PSS is among the most challenging tasks in LED research of the last years. Recently, the substitution of PEDOT:PSS with a layer of MoS₂ nanosheet has been reported to improve the stability of perovskite solar cells [2] and of OLEDs [3] thanks to their non-acidic nature and chemical stability. MoS₂ is a 2D transition metal dichalcogenide studied and applied to a wide range of applications for its superior carrier mobility.

In this work, we prove that solution-processed LEDs using NPLs as emissive material benefit from the integration of exfoliated MoS₂ HIL layer into PEDOT:PSS-free devices. The advantage of such an approach relies on the simplicity of the exfoliation procedure and on the possibility to obtain large area MoS₂ thin films by wet methods (spin-coating). Film morphology and coverage are investigated by means of non-contact AFM, Raman spectroscopy and optical absorption, whereas information on the NPL/MoS₂ interfaces are obtained via time-resolved photoluminescence experiments. The thickness of MoS₂ layer appears to be critical for device performance and ongoing work is focussed on the tuning of the deposition parameters of the MoS₂ nanosheets.

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#202 - A Multilayer Approach To Enhance Charge Injection In Organic Field Effect Transistors

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Other Authors: Alberto D. Scaccabarozzi (Istituto Italiano di Tecnologia), Mario Caironi (Istituto Italiano di Tecnologia)

Organic field effect transistors, OFETs, have attracted extensive interest over the past years thanks to the promise of realize solution-process, flexible and low-cost electronics. Despite all the efforts in optimizing OFETs performances, achieve efficient charge injection from the electrodes is still an open challenge. Such contact performance is the most seriously concern for short-channel devices, with channel length typically less than few micrometres, though they are extremely attractive because of their high-frequency operation and the possibility of high-density integration. In a typical silicon based MOFET, heavily doped regions, close to the Source-Drain electrodes, promote the charge injection. Attempting to reproduce this architecture into organic devices, a wide number of possible methods have been proposed, laying on different doping techniques but mostly of them require high vacuum evaporation and masking systems.

In this work, we present a multilayer structure for the reduction of the injection barrier in Bottom-Contact Top-Gate Field Effect Transistor. A highly doped semiconductor layer - poly{[N,N0-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,50-(2,20-bithiophene)} (P(NDI2OD-T2)) blended with electrically insulating material, high-density polyethylene (HDPE) and doped with dihydro-1H-benzimidazol-2-yl (N-DBI) derivative, act as injection layer while the FET depleted channel is created in an upper layer of pristine P(NDI2OD-T2) formed on top of the previous.

We show, how the addition of HDPE is crucial to overcome the doping diffusion inside the active channel region and in which way OFETs characteristics are enhanced, from contact resistance subthreshold swing. Finally, we will show how this approach can be extended also to p-type organic semiconductors, acting as a versatile method to reduce the injection barrier issue in OFETs.

#203 - A multiscale computational tool for the study of morphology and charge transport properties of heterointerfaces in organic electronic devices

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The development of advanced and multi-functional materials for organic and hybrid electronic and optoelectronic devices is often hampered by the lack of a detailed understanding of property/structure relationship, and especially of the link between molecular structure, nanoscale aggregation and electronic properties. This issue affects particularly interfaces among molecular layers in devices based on thin-film architecture, where the chemico-physical complexity of the system leads to difficult interpretation of experimental results.

In this regard, computational investigations can shed light on the relationship between the morphology at the interfaces and the electronic properties of the materials constituting the organic layers.

In this work, we present the computational tool MIRTO (Modeller of Interfaces and chaRge injection raTes calculatOr). MIRTO represents an integrated multiscale approach able to model the aggregation of organic materials, in realistic environments, at the interface with organic and inorganic substrates, applying Molecular Dynamics (MD) simulations. In addition, the morphologies

obtained are used to investigate the electronic phenomena occurring at the interface by performing Density Functional Theory (DFT) calculations. This framework provides distributions of structural parameters and charge injection rates, enabling the correlation between nanoscale morphologies and charge transport properties in materials constituting the layers of organic devices.

In particular, this tool was applied to two different cases. Namely, morphologies at the interface between a metal and an organic semiconductor were used to compute charge injection rates. Also, we investigated the aggregation of an organic n-type semiconducting material at the interface with graphene.

The approach developed within MIRTO, integrated with experimental validation and characterization, allows the correlation between nanoscale morphology of materials at heterointerfaces, dynamical phenomena and electronic properties, leading to a multiscale computational tool that can be applied to the development and design of advanced materials and devices.

#204 - FAST IN-SITU DEPOSITION AND DESORPTION OF ALKANETHIOLS ON ORGANIC ELECTROCHEMICAL TRANSISTORS

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Surface functionalization by self-assembled monolayers (SAM) is widely recognized as an efficient and powerful approach.^[1] In the field of organic electronics, the formation of SAMs on the surface of semiconductors, dielectrics or electrodes is employed with various purposes: from biofunctionalization^[2] to electronic and morphological tuning of the devices.

Alkanethiols are commonly used SAMs for their ability to bind the surface of gold electrodes, thanks to their thiol head, by incubation of the device in the SAM solution or by a potential-pulse-assisted strategy.^[3]

We applied a potential-pulse-assisted approach for the first time on Organic Electrochemical Transistors (OECTs), printed on polyethylene terephthalate (PET) with a PEDOT:PSS channel^[4], to obtain the functionalization of the gold gate electrode with alkanethiols characterized by various tail groups. We optimized potential, time-step and solution to obtain a fast-in situ deposition of MUA (11-Mercapto-undecanoic acid) on the gate. The presence of the SAM caused the device passivation, which can be exploited, for example, to protect the surface during in-situ functionalization of the channel or to cover the free gate surface after the functionalization with proteins or bioreceptors. We also obtained the full desorption of the self-assembled monolayer by oxidative transfer cycles, which decreased the overall current of the device but made the gate able to be functionalized again.

This strategy could simplify and make faster the formation of self-assembled monolayers in several OECT applications and it also offers a facile desorption approach to recycle the transistors. As a perspective, with our approach we could obtain a fast and selective functionalization of multi-gate devices with specific SAMs.

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#205 - The use of Graphene-based electrodes for nanodevices with low-dimensional materials: from 0D molecular junctions to 1D graphene nanoribbons

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Molecular scale materials are a promising resource for the development of functional devices for the next generation of nanoelectronic components. The key challenge is how to address and exploit them in scalable architectures. Our idea is to use graphene as a suitable material for the realization of the contact electrodes in devices with low-dimensional systems. Indeed, the (2D) planar geometry of graphene reduces the “dimensional mismatch”, optimize the electrical coupling with the gate through reduced screening and allows for the anchoring of a wide variety of molecular compound through specific functionalization.

Here we report our most recent achievements along this line, following two main routes. Firstly, we develop graphene based electrodes which we employ to contact magnetic molecular units. By engineering the gap between graphene electrodes in the nanometer range[1], we demonstrate charge transport through molecules of the TbPc₂ family, in a molecular (spin) transistor geometry. The device is found to be able to measure the coupling between the molecular magnetic moment and the electrical current[2].

Alternatively, we use graphene electrodes to contact atomically precise graphene nanoribbons (GNRs), which represent the ultimate miniaturization of graphene devices with controllable edge properties and functionalities[3]. The resulting “all-graphene” devices show potentialities for optoelectronic applications, including sensitive photo-detection[4]. Finally, we report a systematic study on the structure-property relationship in GNR-based devices, showing that the final electrical behavior is determined by the specific type of nanoribbon employed.

Our results highlights the promising potential of graphene as a suitable template for low-dimensional devices.

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#206 - Hydrogen-driven generation of atomically thin, light emitting domes in transition metal dichalcogenides

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We present the effects of proton (H⁺) irradiation on the structural, mechanical, optical and electronic properties of WS₂, WSe₂, WTe₂, MoSe₂ and MoS₂ (or MX₂) bulk flakes [1].

Protons passing through the top plane of MX₂ flakes trigger the hydrogen-evolution-reaction 2H⁺+2e⁻ → H₂. The ensuing production and coalescence of H₂ molecules leads to the local blistering of the TMD material. As a result, spherical domes form on the surface of the flakes due to the balance between the TMD adhesion forces and the free energy of the trapped gas. The domes are just one X-M-X

plane thick, feature footprint diameter varying between 10 nm and 10 micron, contain highly-pressurized H₂ (ranging from few to hundreds of atmospheres), and are remarkably robust against aging and mechanical stress.

Thanks to their monolayered structure, the domes emit light very efficiently well above room temperature, display circular dichroism and show second harmonic generation signal. The band gap of the domes is at lower energy with respect to that of the planar counterparts due the built-in strain. By finite-element method calculations within the framework of the nonlinear membrane theory, we model the strain tensor components and dome profile, which is in excellent agreement with atomic force microscopy and micro-photoluminescence mapping measurements. The calculations show that the TMD membrane, of which the domes are made, is subjected to high tensile strain (in excess of 5%) that varies over the surface. The peculiar strain distribution allows the unprecedented observation of a direct-to-indirect band gap transition over a curved TMD monolayer. Deformed graphene is also produced by prior-to-irradiation deposition on TMD flakes and characterized by micro-Raman studies.

All these features can be made spatially scalable by exploiting electron-beam lithographic processing. Indeed, the domes can be produced with the desired density, well-ordered positions and size tunable from the nanometer to the micrometer scale, thus providing a template for the manageable and durable mechanical and electronic structuring of two-dimensional materials.

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#207 - Charge transport in reduced graphene oxide thin films: role of the structural (dis)order

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Polymer-composites based on graphene and related materials (GRM), such as thermoplastics and conductive flexible materials, hold promise for several key European industrial areas including aerospace and automotive industries where they find use in coating of batteries and cables, de-icing, etc. The composites of most interest comprise structurally complex membranes of reduced graphene oxide (RGO). These are disordered on multiple length scales and incorporate local geometrical defects, as well as a large amount of functional groups on RGO.

The possibility to produce large quantities of composites, with disordered RGO as the most common filler, is highly relevant for applications [1] but demand a careful optimization of their properties which presently lack guiding rules. Actually, the properties of the produced composites often do not meet expectations. This is attributed to the embedded RGO being disordered on multiple length scales, from the atomic level defects up to sheet boundaries. Presently there is a crucial lack of knowledge in regards to the intrinsic properties of such disordered few-layer RGO, and how it affects charge transport.

Despite of several detailed studies have been performed for single RGO [2] sheets, only few attention has been devoted to thin films and a systematic study is still lacking [3]. Most studies give an ambiguous interpretation of charge transport phenomena by qualitative plot of resistance vs temperature, while a univocal interpretation of the charge transport phenomenon is still object of debate: Efros-Shklovskii variable-range hopping (ES-VRH) or 2D Mott variable-range hopping (2D-VRH).

We perform a quantitative study of the charge transport properties of RGO thin films tuning the structural (dis)order, such as the chemical composition, the film thickness and the lateral size of single sheets. RGO films are described as partially ordered multi-layered networks (random sheet in-plane, parallel stacking out-of-plane). Based on analysis of the reduced activation energy [4], we show that the charge transport mechanism strongly depend on hopping events, following the same physical model in the whole temperature range, the ES-VRH [5].

Moreover, we further correlate the electronic transport mechanisms with the morphology of the RGO film. The probability that charges circumvent the hopping barriers increases with film thickness, with an increase of the localization length of the electronic states up to the micron scale.

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#208 - Tuneable properties on polymeric membranes by layer-by-layer coatings for gas purification and barrier packaging

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Graphene attracted great interest in the membrane field over the last period, due to impermeability to small atoms and molecules combined to extremely high aspect ratio; furthermore, 2D materials open to new viable strategies for mass transport-related applications.

This work shows results obtained by a thin, self-assembled coating produced by layer-by-layer deposition, aimed at the control of the gas permeation rate for oxygen barrier packaging application, and for gas separation membranes (e.g. for hydrogen purification processes). The coating technique makes use of electrostatic species, piled up on a well-ordered stack on top of hydrophilic substrates. This structure results from alternated dip coating process performed with diluted aqueous dispersions, where substrate is first immersed in electropositive polyelectrolyte solution and immediately rinsed with water, in order to promote a thin well-ordered structure by removing polymer excess and inhomogeneity. First-layered sample is then immersed in diluted graphene oxide (GO) suspension to cover the outer surface with an atomic-thick graphene layer, then water rinsing is performed for excess graphene washout. A multilayer structure is then grown by repeating the alternated dip coating process up to a prescribed number of flat thin double layers.

An advanced scanning ellipsometry technique is here used to show micromaps for each building layer, and to demonstrate the high structural order obtained by layer-by-layer, as well as to evaluate the thickness of each layer, compared by common scanning electron spectroscopy performed on cross section of coated silicon wafer. Typical thickness results obtained are 2.3 ± 0.2 nm for polyethylene imine layer (partially-charged polycation) and 1.4 ± 0.2 nm on average for GO layers. The latter value results incredibly close to the GO monolayer sheet thickness, previously measured by atomic force spectroscopy on single sheets.

Multiple positive polyelectrolyte with varied steric properties are used in order to control gap between subsequent GO layers, and different transport properties to gaseous species is expected due to a different volume available to molecules for diffusion phenomenon, and also a different path geometry they are forced to go through. Gas permeability values of helium, hydrogen, carbon dioxide and oxygen are then reported, showing interesting values for specific applications. As example, 96% reduction of oxygen flux through commercial PET can be obtained by a 25 dips process, or hydrogen/carbon dioxide selectivity values up to 300 can be easily attainable with commercial polyimide films when coated. Permeability measurements are also used as a powerful tool for structural characterization of self-organized structures, which shows a clear molecular-sieving behaviour, sensitive to GO treatments.

#209 - Dynamical processes at surfaces imaged by STM on the millisecond time scale: the FAST module

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Dynamical processes occurring at surfaces, such as surface diffusion, film growth, self-assembly and chemical reactions, typically occur at the millisecond or smaller time scale and their characterization thus makes necessary the use of experimental techniques providing a comparable time resolution. Moreover, the full comprehension of this processes requires their investigation at the atomic level within the same time scale. Scanning probe microscopy (SPM), which allows the imaging of surfaces on the nanometer size, on the other hand is usually characterized by severe limitations on the achievable time resolution, since the typical image acquisition times are of the order of few seconds or more. To overcome this limitation, we developed the FAST module, an add-on instrument that can drive commercial SPMs at and beyond video rate frequencies in a totally transparent way, requiring no modification of the existing scanner hardware and electronics [1, 2]. Here we present a selection of high-speed STM measurements (up to 100 frames per second) obtained coupling this device to commercial SPMs, highlighting the need of this time resolution in studying dynamical processes such as the growth of graphene edge on Ni(111) at 470 °C [3], the dynamics of Fe₃O₄(001) surface and the self assembly mechanism of molecular networks at 77K and RT [4]. Finally some technical details on the functioning of the FAST module will be given.

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#210 - Artificial anisotropy in CVD-grown MoS₂ Nanosheets: from morphology to opto-electronic properties

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Morphology and physical properties are mutually cross-related in two-dimensional (2D) materials. As a consequence, the manipulation of the spatial profile in 2D nanosheets is a promising way to trigger novel functional properties. In 2D MoS₂ a modification of the electronic bandstructure can be induced at the local scale by mechanically wrinkling the nanosheets. As a consequence, the anisotropy of the spatial deformations introduces an additional degree of freedom for the functionalization of the opto-electronic response along arbitrary spatial directions [1].

Here, taking advantage from highly conformal chemical vapor deposition (CVD) approach, we forced MoS₂ nanosheets i) to replicate an anisotropic rippled profile and ii) to form laterally confined nanostripes in nanopatterned substrates [2,3]. We show that, in both cases, the anisotropic morphology dramatically affects the opto-electronic properties of MoS₂. Localization of strain and charge modulation are observed at the nanoscale as a function of the surface profile modulation, causing substantial red shifts of the phonon mode frequencies and a topography-dependent distribution of the electronic workfunction, respectively. At the macroscale, a strong anisotropic redistribution of the phonon scattering intensity is observed for orthogonal orientation of the incident polarization. Furthermore, ultrafast transient optical spectroscopy shows a polarization dependent response for the electron-phonon scattering decay and hints at the possibility of anisotropy-related exciton engineering [4].

Our approach paves the way to a controllable and versatile tuning of the physical properties at the 2D level via substrate pattern design. A wealth of technological fields, ranging from nano-photonics and electronics to catalysis, may benefit from the anisotropy engineering of 2D materials [5].

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#211 - Decoupling Graphene from Ni(111) through the Intercalation of a Chromium Carbide Ultra-Thin Film

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During the last decade, graphene has been stabilized on many single crystal metallic substrates [1]. Among them, the Ni(111) surface represents an ideal template for the epitaxial growth of graphene, because the excellent lattice matching between the two materials promotes the stabilization of large-area and defect-free honeycomb monolayers. However, the hybridization between the Ni d bands and the graphene π states strongly modifies the electronic structure of the latter around the Fermi level. In order to obtain a quasi-freestanding graphene layer, metallic films have been intercalated between graphene and the substrate [2].

In this framework, it is reasonable to assume that an even better decoupled carbon monolayer could be obtained by intercalating insulating compounds such as carbides, oxides or nitrates [3]. Traditional techniques, such as surface exposure to a reactive gaseous environment, are not suitable to stabilize insulating compounds underneath the honeycomb monolayer, because the highly impermeable graphene membrane hinders the chemical reactions between the gas and the metal. Here, we demonstrate that it is possible to grow an ultra-thin Cr carbide between graphene and Ni(111). Auger electron spectroscopy reveals that the deposition of Cr on the graphene/Ni(111) system triggers, upon intercalation of Cr, the segregation of C atoms from the bulk of the Ni substrate, inducing the development of a crystalline Cr carbide at the interface [4]. The atomic structure of the graphene/Cr carbide/Ni(111) system has been investigated by means of Low Energy Electron Diffraction and Scanning Tunneling Microscopy. Moreover, Scanning Tunneling Spectroscopy suggests that the intercalation process restores the linear dispersion of the energy bands characterizing the freestanding graphene. Further Angle-Resolved PhotoEmission Spectroscopy (ARPES) measurements will be presented, in order to clarify this last issue.

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#212 - Innovative transmission electron microscopy for plasmonic nanostructures: probing the charge symmetry and transverse fields at the nanoscale

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Plasmonics, the science and technology of the interaction of light with metallic objects, is fundamentally changing the way we can detect, generate and manipulate light. The field is progressing swiftly, thanks to the availability of nanoscale manufacturing and analysis methods, among which transmission electron microscopy (TEM) and in particular electron energy loss spectroscopy (EELS) is very popular due to being the first technique able to detect and image the dramatic variations in the electrical field of the induced resonances of a single nanoparticle. Despite its great success, the standard experimental setup does have limits, and only allows to qualitatively image the intensity of the electrical field projected along the beam direction. While optical spectroscopies can make use of polarisation to directionally probe the response of a particle, an electron beam can't discriminate between energy-degenerate eigenmodes and is also blind to optical activity and dichroism. Here two new approaches are presented, expanding the wealth of information that can be extracted through a commercial TEM.

In the first method, we manipulate the wave function of the electron beam to selectively detect only excitation with a chosen symmetry of the charge density [1]. Beside allowing to probe the charge symmetry, this approach allows to devise special beams that reproduce the selectivity properties of linearly or circularly polarised light.

In the second one, measuring the deflection of inelastically scattered electron allows to quantitatively probe the transverse fields of the induced resonances [2]. This finally allows to probe all three components of the electrical field in a TEM, and paves the way to the direct tomographic reconstruction of the three dimensional shape of the field.

Both methods are introduced, then demonstrated with simulations and experiments.

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#213 - Nonlinear photonics on single plasmonic nanomaterials at the nanoscale

Paola Borri (I) - Cardiff University

Metallic (plasmonic) nanomaterials are attracting increasing interest for many applications in photonics, ranging from optoelectronic devices and photovoltaics to bioimaging and biosensing. An advantage of these systems is that their optical properties, governed by their localized surface plasmon resonance, are widely tunable with the nanostructure shape and size. Notably, for many applications, it is essential to have a quantitative knowledge of the linear and nonlinear optical properties of the individual nanostructure at the nanoscale, beyond traditional ensemble-averaged measurements.

At Cardiff University, we have pioneered the development of linear [1] and nonlinear [2] optical microscopy techniques of single plasmonic nanoparticles, and shown their general applicability to other nanoparticles including nanodiamonds [3]. In terms of nonlinear light-matter interaction, four-wave mixing (FWM) triply-resonant to the localised surface plasmon was shown by us to be a very selective, high-contrast, photostable method to detect single small gold nanoparticle down to 10nm diameter [2]. FWM is a third-order nonlinearity which originates from the change in the nanoparticle dielectric constant induced by the resonant absorption of a pump pulse and subsequent formation of a nonequilibrium hot electron gas in the metal [3]. It is therefore very specific to a metallic nanoparticle which can be imaged completely background-free even in a highly scattering and fluorescing environment. Notably, the technique also provides a new method to determine the position of the nanoparticle with nanometric precision in 3D from scanless far-field optical measurements [2]. Furthermore, it is uniquely sensitive to particle asymmetries of only 0.5% ellipticity, corresponding to a single atomic layer of gold, as well as particle orientation. This method opens new ways of unravelling single-particle trafficking within complex 3D architectures, and holds great potential for correlative light-electron microscopy. Its application to novel plasmonic materials including single nanohelices will be presented.

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#214 - Plasmonic nanostructures for sensing and imaging*Isabel Pastoriza-Santos (I) - University of Vigo**Other Authors: Plasmonic nanostructures for SERS-based applications*

The novel field of Nanoplasmonics focuses on the manipulation of light using materials with significantly smaller sizes than the radiation wavelength. This is typically achieved using nanostructured metals, since they can very efficiently absorb and scatter light due to their ability to support coherent oscillations of free (conduction) electrons. The great development of Nanoplasmonics is based on the fine control over the composition, size and morphology of nanostructured metals. Particularly, wet-chemical methods have the advantage of simplicity and large-scale production, while offering a number of parameters that could determine the final particle morphology and surface properties, which is essential for the further processing. This seminar will provide an overview of recent developments of the *Colloid Chemistry Group* in the Nanoplasmonic field with special emphasis in SERS based imaging and sensing.

#215 - Extremely Close Gap Aluminum Bowtie Nanoantennas Fabricated by Helium Focused Ion Beam for Plasmonic Applications in the Visible Range*Massimo Cuscunà - CNR-NANOTEC, Istituto di Nanotecnologia*

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Plasmonic bowtie nanoantennas are intriguing nanostructures, capable to achieve very high local electromagnetic (EM) field confinement and enhancement in the hot spots [1,2]. This effect is strongly dependent on the gap size, which in turn is related to technological limitations. Ultra-narrow gap bowtie nanoantennas, operating at visible frequencies, can be of great impact in biosensing applications and in the study of strong light-matter interactions with organic molecules.

In the present work we report a simple and robust way to produce extremely close gap Al bowtie nanoantennas with gap ranging from 10 nm, by electron beam lithography (EBL), down to 3 nm combining EBL and Milling-based He⁺-ion lithography (HIL). Furthermore, we present our findings on the stability of extremely close gap Al dimers when exposed to indoor air at ambient conditions. This analysis demonstrates that large EM near-field enhancement and different hot spot spatial positions, as a function of nanometer-sized gaps, are constrained by the native aluminum oxide, thus working as hot spot ruler.

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#216 - Effective dielectric modelling of hot gold nanoparticles*Michele Magnozzi - OptMatLab, Dipartimento di Fisica, Università di Genova*

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Metal nanoparticles (NPs) have the interesting property of behaving as efficient converters of EM radiation into heat. While this can occur via interband photoexcitation, the presence of a Localized Surface Plasmon Resonance provides an extra degree of freedom to tune and optimize the heating [1].

Assessing the temperature of plasmonic NPs during or immediately after illumination is not an easy task, and typically involves the use of models that necessarily have to simplify the complex temperature-dependent dielectric and thermodynamic response of nanosystems; for this reason, a measurement of the T-dependent optical behavior of the NPs at well-defined, externally controlled T would greatly contribute towards a better understanding of the thermoplasmonic properties of metal NPs.

Spectroscopic ellipsometry (SE), being a high-sensitive and non-destructive technique, is an ideal tool to investigate the optical response of NPs systems, provided that a proper model is used for data analysis. We report a T-dependent investigation of the optical response of densely-packed 2D arrays of gold nanoparticles supported on an insulating nanopatterned substrate [2]. SE measurements were acquired in the 245-1450 nm

spectral range, under high-vacuum conditions and in the 25-350 °C temperature interval [3]. Using a dedicated effective medium approximation developed for this kind of systems [2], we are able to reproduce the complex anisotropic optical response of this system employing morphological parameters deduced by ex-post AFM analysis; the temperature-dependent dielectric functions of Au, required as input in the model, was obtained in a dedicated SE measurement. The model yields a very good agreement with experimental data at relatively low T; however, though the appropriate T-dependent dielectric function of Au is systematically employed, the model is no longer able to reproduce the data obtained at the highest T. Indeed, a satisfactory agreement is attained introducing an effective

correction to the Drude term of the dielectric function of Au, that keeps into account morphological effects affecting the NPs surface - such as softening or melting - that enhance the surface electron scattering rate. Our analysis thus show that the T-dependent optical properties of metal NPs deviate from simplified expectations, and validate SE as valuable tool to study the complex, anisotropic properties of plasmonic NPs systems.

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#217 - Interaction and coherence of a plasmon-exciton polariton condensate

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Hybrid particles of excitons in semiconductors and cavity photons, called polaritons, have shown fascinating phenomena including Berezinskii-Kosterlitz Thouless transitions and Bose-Einstein Condensation (BEC) recently observed at room temperature in organic-based microcavities [1]. In this context, a promising route for the exploitation of polariton physics at the nanoscale is offered by the Surface Lattice Resonances (SLRs) arising from the coherent radiative coupling of diffractive modes, propagating in the plane of an array of metallic nanoparticles, with the localized surface plasmons (LSP) of each individual nanostructures [2]. The SLR systems showing a high electromagnetic (EM) field enhancement are characterized by a strong suppression of losses (higher quality factor) with respect to individual nanoparticle LSPs, at the expense of a less confined electromagnetic field (larger mode volume) [3]. By strongly coupling molecular excitons to a SLR in a 2D array of silver nanorods (NRs), we demonstrate the formation of an out-of-equilibrium plasmon-exciton-polariton (PEP) condensate with an extended spatial coherence over distances longer than the excitation spot. This is proved by time resolved experiments which evidence the picosecond dynamics of the condensate and a sizeable blueshift, thus measuring, for the first time, the effect of polariton interactions in plasmonic based cavities. These findings are very promising for studying properties of quantum fluids at room temperature with ultrafast dynamics, thus opening the way towards future plasmon-exciton-polariton based condensates and devices.

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#218 - Plasmonics with refractory TiN

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Using First Principles calculations we study the optoelectronic properties of Titanium Nitride, a refractory compound that has been proposed as a feasible route to substitute gold in harsh environment applications. [1]

The microscopic origin of the plasmon resonances and their dispersions are discussed on the basis of the analysis of the electronic structure and of the interplay between collective and single-particle excitations, which determine the screening and dissipation effects of the electronic system. [2] We furthermore analyze different interfaces between TiN and conventional semiconductors in order to describe TiN surface-plasmon polaritons for the realization of hyperbolic metamaterials and waveguides.

We also investigated the optoelectronic characteristics of the compound in relation to the crystal phase transition, experimentally observed at very high pressure. From the simulation of energy-loss spectra at different momentum transfer, we derive the TiN plasmon dispersion relations that are directly accessible by experimental measurements.

The effect of confinement in ultrathin TiN films is explored. [3]

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#219 - From laser cladding to laser metal deposition: challenges in the laser-aided direct energy deposition process for 3D printing of metallic parts.

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Laser Metal Deposition (LMD) utilizes a concentrated laser heat source, with in situ delivery of powder (or wire) for subsequent melting to accomplish layer-by-layer part fabrication. LMD can be used to generate functional parts via layer-wise cladding, providing an opportunity to generate complex-shaped, functionally graded or custom-tailored parts. This has great potentiality when single-piece or small batch size large components, traditionally produced by casting or forging, are requested. Often, these parts are requested in sectors, as aerospace, energy and transports, where Ni, Al and Ti based alloys are used. LMD has been investigated heavily in the last several years as an additive method for producing large parts in high performing metallic alloys but several barriers have hindered the diffusion of this process at the industrial level.

This work gives an overview of most recent results in LMD of large components and explores challenge points of this subject: flammability and safety; automation and CAD-CAM integration; qualification of mechanical properties the bulk and surface and process monitoring and control.

#220 - Nanowires for Phase Change Non-volatile Memories

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Interest in phase change random access memory (PRAM or PCM) devices as future high performing, non-volatile and non-charge based memory devices is increasing. They offer high-speed operation, endurance and downscaling, even beyond lithographic limits, so that they are emerging as a leading contender for storage class memories that should fill the performance gap between volatile DRAM and non-volatile Flash memories [1]. The first PCM devices were commercialized in 2010 by Micron (a 128 Mbit device) and by Samsung (a 512 Mbit device). Currently downscaling is in progress, as confirmed by the recently announced “3D XPoint” technology from Intel and Micron [2], which is purported to be based on phase change materials, typically chalcogenides of the Ge-Sb-Te system.

One viable route to further scale down and improve the PCM memory device performances is the use of self-assembly processes by chemical deposition methods, such as chemical vapor deposition (CVD), to produce low-dimensional phase change nanowires (NWs) as memory cells, since their growth can be controlled, along with their diameter, composition and crystallinity [3]. Among the CVD methods, the metalorganic chemical vapor deposition (MOCVD) is featured by high process control, large area deposition and industrial transferability, but the process to synthesize chalcogenide NWs has very narrow deposition conditions.

In this presentation, after an introductory overview on nanostructures for PCM, the MOCVD self-assembly of the (In-Ge-Sb-Te) system and core-shell Ge/In-Te NWs performed at the Agrate Unit of CNR-IMM will be illustrated [3,4,5], followed by very recent results on Sb₂Te₃ NW positioning control in patterned substrates. The chemical-physical properties of the grown NWs will be reported and the memory functionality of the related NW-based memory test devices will be demonstrated by programming current, switching speed, power consumption, and compared with the state of the art results.

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#221 - Bioinspired artificial Salvinia-like patterns for air trapping and drag reduction via direct laser lithography.

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Biomimetics focuses on the study of natural systems to find out the inspiration for technological issues for which nature has already developed a solution. The characteristic of the biomimetic paradigm is the deep connection between materials and morphology: with

a relatively small number of structural materials and by exploiting proper morphologies, nature has been able to achieve very complex functionalities.¹

Salvinia Molesta is a fern that has found a strategy for the long term retainment of air on its leaves when it is submerged by water: the 'Salvinia effect'.² This result is achieved thanks to a chemical coating and to the three-dimensional and hierarchical shape of the hairs covering the leaves: the hairs are composed of a stalk (about 1 mm long) capped with a crown-like head, made by four filaments, of about 500 μm in height. The apex of the filaments is composed of smooth dead cells, providing a pinning point for the water droplets, while the rest of the hair is covered by hydrophobic wax crystals.

Starting from the natural model, we microfabricated hairs inspired by Salvinia leaves, replicating both the geometry and the chemical characteristics. We focused on the wettability and the pinning capability since these two aspects are deeply involved in the air retention mechanism and drag reduction.

Salvinia hairs were reproduced in a hydrophilic photoresist (IP-S, Nanoscribe GmbH) about 10 times smaller than the natural counterpart by means of two-photon lithography.³ Three different geometries were reproduced by changing the number of filaments of the heads. The samples were covered with a nanometric layer of Teflon. Part of the samples were further modified making the tips of the heads hydrophilic by depositing a small amount of photoresist *via* micro-imprinting.

Roll-off and static contact angles were measured to describe the wettability characteristics and compare the effect of the geometries on the performances. The presence of Teflon was able to induce super-hydrophobic behavior with a contact angle of 170° and roll-off angle of 10° . The patterns with a fully bioinspired chemical treatment (selectively hydrophilic tip on the overall hydrophobic structures) restored the droplet pinning capability. They showed a static contact angle of 160° , but they were able to properly pin the water, showing a roll-off angle well above 40° . This results are promising for the study of the drag reduction properties of such type of patterned surfaces.

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#222 - S-parameters characterization of high-frequency organic transistors

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The maximum operational frequency of OFETs is going to increase thanks to constant improvements in polymers charge carrier mobility. Since the frequencies of transition that has been achieved nowadays are in the order of tens of MHz, the direct measurement of transistor performances becomes not trivial because of parasitic contributions or the occurrence of resonance.

In this work, a setup for scattering parameter measurement is installed, allowing reliable measurements up to 10 GHz. A process compatible with S-parameters measurement is demonstrated. OFETs are realized through a mask-less approach, combining a fs-laser process for the sintering of high resolution metal electrodes and suitable deposition technique of high mobility polymer semiconductor. OFET frequency behavior is characterized using S-parameters, highlighting the trend of the transition frequency as a function of the channel length.

#223 - Controlling the 2-photon optical creation and growing of gold nanoparticles

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Two-photon direct laser writing (TP-DLW) in polymeric matrices doped with tetrachloroauric acid (HAuCl_4) solution allows to create clusters of gold nanoparticles (GNPs) inside the focus figure of a tightly focused laser beam. Here, we present the analyses made on some key physical phenomena involved in the process, beyond the bare optical absorption. The two-photon absorption (TPA) triggers the photo-reduction of AuCl_4^- ions and the creation of GNPs, but to a local heating of the sample as well, which generates a thermal shock-wave, responsible for the local dehydration of the spotted volume. Due the concentration gradients of the gold precursor and of water, different diffusive processes take place, occurring on different timescales. Here, it is demonstrated that the diffusive effects can be exploited for controlling the NPs density and dispersity in size when a given energy dose is delivered in multiple shots, by tuning the time interval between each shot and we developed a very simple while effective technique to get an estimation of the temperature distribution reached during TP-DLW. Moreover, some experiments revealed the role of the surface affinities between the GNPs, the substrate and water, demonstrating the possibility to create clusters rich in gold nanoparticles in the bare chloroauric solution, avoiding the polymeric matrices.

The different analyses performed pointed out that, in order to get best control on the GNPs photo-reduction, thermal effects have to be reduced, while a fine control on the ionic concentration is required. We prepared electrolytic cells made of Glass plated coated with ITO transparent electrodes, in which a very diluted solution of HAuCl_4 in water was infiltrated and we printed stripes of GNPs at an energy dose sufficient to activate the seeding process of TP-photo-reduced gold ions. Because of the low ionic density, the growing process of GNPs is inhibited.

Growing of gold nanoparticles was then performed by applying an electric potential difference between the two electrodes, well below the electro-chemical reduction threshold, in order to increase the ionic concentration close to the boundary surfaces. We verified the presence of two ionic species involved in the reduction process (AuCl_4^- and Au^+). The electric field allows controlling the surface density of the ionic species of interest, both for the seeding and the growth phases. Regarding the last, we consider that in proximity of a gold seed a tip effect is obtained, “driving” the gold ions toward the seed rather than the ITO electrode, where they are reduced through auto-catalytic processes. Analyses on the stripes confirmed a voxel size comparable to the laser beam waist, and that the gold nanoparticles TP-photo-reduced are mono-dispersed, demonstrating that the proposed electrophoretic method is effective in controlling the local ionic concentration and hence the GNPs density and size.

#224 - Flexible, large-area ionizing radiation detectors based on organic semiconductors

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A new generation of ionizing radiation sensors based on organic materials is attracting a large attention exploiting appealing features of such as ease of processing, low power supply and mechanical flexibility. Moreover, the equivalence of the typical density of organic molecules to that of human tissue makes them very suitable for medical X-ray direct dosimetry.

In the field of ionizing radiation detection, organic materials have been mostly employed so far in indirect radiation detection systems, either as scintillating material or as (organic) photodetectors.

Our approach is based on the use of organic semiconductors as the active material for the direct detection of ionizing radiation, implementing real-time and room temperature operating sensors. In the last years, a few works reported the proof-of-principle for direct X-ray detection based either on organic semiconducting single crystals [1] or on polymer thin-films blended either with π -conjugated small molecules, inorganic high-Z nanocomponents [2] to enhance the sensitivity to X-rays improving the charge carriers mobility and the stopping power of the material.

We realized direct, lightweight detectors based on micro-crystalline thin films of TIPS-pentacene deposited by inkjet printing onto flexible substrates and we assessed their high X-ray sensitivity (up to several hundreds of nC/Gy at ultra-low bias of 0.2 V). We investigated the direct X-ray photo-conversion process in order to interpret the detection mechanism and we developed a kinetic model that gives an important insight into the physical process that leads to highly sensitive response to ionizing radiation by such low-Z organic materials.

Finally, we assessed the possibility to use the detector under mechanical strain and gave the first demonstration of a 2x2 pixelated matrix organic detector [3].

These results open the way for novel flexible, large area and low voltage ionizing radiation detection systems, capable of providing quantitative and real time information on the dose rate and on the spatial distribution of impinging radiation.

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#225 - Improved discrimination of target gas molecules by specific humidity monitoring of a nanostructured platform based on functionalized SWCNT for breathonomics applications.

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Breath testing (or breathonomics) allows the analysis of the most common volatile organic compounds (VOCs), and it is expected to be a non-invasive and a real-time monitoring technique. The effort to develop methods and devices for breath analysis is quite intense nowadays, and, among the devices for breath testing, electronic noses may become an important resource in the diagnostics of some diseases (e.g. lung cancer, cystic fibrosis, liver or kidney failure...), or in health screening programs.

An array of 8 CNT sensors, functionalized with organic molecules (TCTA, PANI, TAPC, PTCDA, COOH, DNA, Hex-4T-Hex), has been produced to explore applications in the field of breathonomics. The array was exposed to a set of target gas molecules relevant to specific diseases (e.g. NH₃, NO₂, H₂S, benzene, acetone, ethanol...), and the data analysis was carried out on the basis of the principal component analysis (PCA) approach. The results show that this array of sensors can detect different target gas molecules, with clear tracks on a 2D PCA subspace. We demonstrate that the capability of discrimination is further enhanced when a specific humidity sensor is added, improving the overall array selectivity. Moreover, preliminary tests on the exhaled breath from 3 volunteers has been carried out and the capability to discriminate the breath fingerprint of each volunteer has been demonstrated. The results show that the device can be regarded as a promising platform for the implementation of an electronic nose for breathonomics, with active layers deposited on flexible plastic substrates and operating at room temperature.

#226 - Organic Transistor Biosensors for biomarkers and pathogens

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Bio-recognition is a fundamental mechanism in biological processes in living systems, and it is widely exploited in technological and health applications. Organic Electronics is an emerging technology perfectly suited to connect electrical and biological worlds, thanks to biocompatibility of many used materials, capability of working in liquid environment, flexibility and ease of fabrication. Moreover, one of the main innovative feature of Organic Electronics is the idea that materials properties of the different components can be selectively tuned through chemical modification or designed synthetic procedures. The presented work is focused on the functionalization of the gate electrode in Electrolyte Gated Organic Field-Effect Transistors (EGOFETs) in order to obtain specific biosensors working in liquid environments.

A number of functionalization strategies have been tested towards several biological targets: here are demonstrated two strategies based on monoclonal antibodies or peptide aptamers as sensing moieties immobilized on the gate surface, and the performances of the obtained biosensors towards really different targets.

The sensor behavior has been demonstrated towards small human proteins (few kDa molecular weight) of the cytokines family with well documented roles in inflammation, apoptosis, proliferation, angiogenesis, metastasis and morphogenesis. The EGOFET sensors have shown to work in simple buffered solutions as well as in real samples and exhibited a super exponential response below the nM range.

Subsequently, the sensor has been tested in the detection of small molecules in solution: the sensing moiety immobilized on the gate is a Histone demethylase, a protein involved in several tumor pathologies without known therapies. In a view of using EGOFETs as tool for drug discovery, we tested the sensitivity of the sensor towards different demethylase inhibitors.

Lately the biosensor has been tested towards a larger target: Plum Pox Virus (PPV), one of the most aggressive viruses of fruit trees, which dimensions are in the hundreds of nm range. We exploited polyclonal antibodies anti-PPV as sensing moieties on the gate electrode and detected increasing PPV concentrations in plant extracts.

This work demonstrates the feasibility of EGOFETs biosensors towards really different kinds of analyte, ranging from small molecules to big plant viruses, and the possibility of using the device to study the thermodynamics of biomolecular recognition between immobilized moieties and target analytes in solution.

#227 - Ultra sensitive non-electrochemical detection of Dopamine in model solutions

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We demonstrate the ultra-sensitive and selective detection of dopamine (DA) by means of a neuro-inspired device platform without the need of a specific recognition moiety. DA is a neurotransmitter of catecholamines family that controls functions of cardiovascular, renal, hormonal and central nervous systems. DA deficit is a hallmark of Parkinson's disease (PD), due to the degeneration of dopaminergic neurons in *substantia nigra pars compacta*. The sensor is a whole organic device featuring two electrodes made of poly(3,4-ethylenedioxythiophene):polystyrene sulfonate – PEDOT:PSS – directly patterned through laser ablation on a polydimethylsiloxane – PDMS – flexible substrate. One electrode is pulsed with a train of voltage square waves, to mimic the pre-synaptic neuron behavior, while the other is used to record the displacement current, mimicking the post-synaptic neuron. The current response exhibits the features of synaptic Short-Term Plasticity (STP) with facilitating or depressing response according to the stimulus frequency. We found that the response characteristic time t_{STP} depends on DA concentration in solution. The sensor detects [DA] down to 1 pM range. We assess the sensor also in the presence of ascorbic acid, uric acid, homovanillic acid and 3-methoxytyramine, which are all physiologically present in cerebrospinal fluid. Our detection strategy successfully discriminates DA from the other analytes in model solutions (i.e. Phosphate Saline Buffer) containing increasing concentrations of the analytes, ranging on nine orders of magnitude (from 1pM to 1mM). The selectivity of the sensor was also tested in operational conditions nearer to the *in vivo* ones creating mixed solutions with the physiological concentration of one of the four analytes and increasing concentration of DA. The sensor appears still more sensitive to DA than to the others, even with similar chemical structures. The synapse appears ultrasensitive to DA (from physiological to pathological concentrations) and selective thanks to the interaction mechanism between analytes and PEDOT:PSS. The whole organic synapse, being biocompatible, soft and flexible, is attractive for implantable devices aimed to real-time monitoring of DA concentration in bodily fluids, to be used as a diagnostic tool, for instance, in chronic neurodegenerative diseases such as Parkinson's disease.

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#228 - Charge transport processes in organic electronic photocapacitors for neuronal stimulation

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Stimulation of neurons in a localized and safe manner is important both as an investigative tool and as a therapeutic means. Optoelectronic wireless stimulation has evolved in recent years as an inherently less invasive alternative to wired microelectrodes. Material science and physics are requested to investigate novel semiconducting materials that achieve the transduction of light into an electrolytic current signal, strong enough to depolarize attached neuronal cells. Organic Pigment photocapacitors have been recently discovered as efficient nanoscale semiconducting optoelectronic system for such neuronal stimulation. (1) The organic p-n junction based thin-films are biocompatible and avoid electrochemical reactions giving rise to a purely capacitive electrolytic current. In this study we investigate the basic mechanism of charge separation and transient current formation by photo-electrochemical current spectroscopy and microscopic surface voltage characterization exploiting optically excited Kelvin Probe Force Microscopy. Our findings elucidate the role of the thin films microstructure on the transient electrolyte current signal. Based on the experimental data, we propose a microscopic model that rationalizes current intensities and timescales observed in electrolytic photocapacitors, both crucial parameters to achieve highly efficient remote neuronal stimulation.

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#229 - Infrared laser photostimulation elicits calcium signaling in primary differentiated rodent astrocytes

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Infrared neural stimulation (INS) has been shown to be an efficient label free optical method to stimulate/modulate firing of neuronal cells and display huge potential for understanding brain physiology and for the cure of pathologies of the Nervous System. Astrocytes water and ion channels and calcium signaling has demonstrated that they play a key role in brain physiology and pathophysiology. However, besides the ability of INS to investigate/modulate astrocytes protein channels and Ca^{2+} signaling in vitro and its mechanism behind it remained to be investigated¹. Here, we investigate the effect of INS on intracellular Ca^{2+} dynamics of astrocytes. We found that INS elicit Ca^{2+} signaling in primary rat cultured astrocytes grown on Poly-D-lysine. When astrocytes were grown on hydrogels, (HTlc), a validated cell culture model of differentiated primary astrocytes², INS can activate Ca^{2+} activity in astrocytes cell body and microdomains. Besides, we investigate the initiation and propagation of intracellular Ca^{2+} rises, identifying a role of extracellular calcium by using siRNA technology, pharmacological tools and Knock out models that enable to propose a novel hypothesis for describing the mechanisms underpinning the effect. Collectively, these results pave the way for the use of INS to modulate astrocytic biophysics not only at cellular but also at subcellular scale.

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#230 - Nanoparticle- semiconducting polymer composites for a new chemical sensor

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Nowadays, great research efforts are devoted to develop biosensing systems able to continuously not-invasively monitor the health state and physiological parameters of humans. The analysis of concentrations of ions in sweat is crucial for several health conditions. In particular, the evaluation of Chloride concentration in sweat for infants and children is a method to diagnose Cystic Fibrosis, a genetic disease that causes persistent lung infections. Moreover, the presence of different ion concentrations in sweat can be directly related to dehydration and a correct monitoring of the biofluids while training can help athletes to increase their performance. The main bottleneck for developing non-invasive ions sensing is the large amount of sample sweat needed for such analyses and the sensitivity and portability of the sensing system.

Here we report a new sensor inspired by the organic electrochemical transistor (OECT), based on a composite material of PEDOT:PSS (poly(3,4-ethylenedioxythiophene) poly(styrene sulfonate)) and $\text{Ag}/\text{Ag}_n\text{X}$ nanoparticles, where X refers to the ion to be detected in

sweat (Cl^- , Br^- , I^- and S^{2-}). The Ag/AgX NPs act as a gate electrode embedded into the conductive polymer channel, thus combining an intrinsically amplified response with a simple two terminal electrical connection. To demonstrate our strategy, we focus our investigation on the Ag/AgCl NPs PEDOT:PSS composite. We demonstrate that the spontaneous interaction between the NPs and Cl^- ions present in the sample solution is directly coupled to the charge transfer process into the semiconductor. Consequently, the current flowing in the channel is directly related to the logarithm of Cl^- concentration. The NPs embedded into the conductive polymer induces a faster sensor response (15 ± 3 s) respect to the corresponding OECT (118 ± 8 s).

The here reported new two terminal configuration biosensors can operate sampling only a few microliters of sweat. We have also implemented such a sensor as a fully textile electronic device, fabricated directly onto a cotton yarn for real-time sweat monitoring.

#231 - Organic electrochemical transistors (OECTs) for smart monitoring of cell stress condition in leaky-barrier cell lines

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Semiconducting polymers are very promising materials for biomedical application, thanks to the ability to conduct both ions and electrons, their biocompatibility and their flexible and soft mechanical properties. In particular, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) has high conductivity, electrochemical and thermal stability in aqueous environment and low oxidation potential that renders it suitable as smart nano-interface with biological elements and environment.

In our work, we present PEDOT:PSS-based Organic Electrochemical Transistors (OECTs) for the electrical continuous monitoring of tissue culture viability, growth and stress response induce by drug treatment, providing an alternative and real-time way to standard optical evaluation techniques, which often require complex instrumentation and laboratory protocols. In OECTs, the electronic current flowing in the conducting polymer channel is modulated by the ionic current crossing the interface with an electrolyte solution (cell culture medium). The presence of a cell monolayer, directly grown on the semiconducting channels and gates of our devices, slow down the ions flowing in the conducting polymer, thus giving an electronic readout of the layer integrity and health. Moreover, the transistor configuration enhances the sensitivity due to amplification of the ionic current. Finally, changing the dimensions of the device and switching between its two configurations, renders it suitable for different kind of cells, allowing even the study of leaky-barrier or non-barrier cell lines.

We demonstrated that our devices provide a simple, low-cost and dynamic method to monitor cell viability and reactions to toxic agents of CaCo-2 and NIH-3T3 cell lines, paving the way for high throughput and low-cost screening of drug discovery or toxicology.

#232 - Strongly-bound excitons in Organic-inorganic 2D Perovskites: a DFT + post-DFT study

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Organic-Inorganic Halide Perovskites (OIHPs) represent the most relevant breakthrough in the last decade in photovoltaics (PV). [1] Nowadays solar devices based on this technology show astonishing conversion efficiencies over 22%. [2] 3D OIHP superior features as light harvester in photovoltaic (PV) devices stem from a wide range of unique properties: high compatibility with solution-based processing, good efficiencies due to a high absorption coefficient, and gaps ideal for single-junction solar cells are only few of such appealing properties [3].

Despite so many attractive features, there remain some serious issues that prevent their usage in device mass production. The most detrimental is undoubtedly the fast air/moisture induced degradation of OIHP cells [4]. For this reason, in the last years two-dimensional Ruddlesden-Popper perovskites (2D-RPPs) have emerged as an alternative to 3D bulk for their superior photo- and chemical-stability coupled with high-performance opto-electronic devices and an enhanced hydrophobic nature of the organic part. These layered materials have a general formula of $(RNH_3)_2(CH_3NH_3)_{n-1}B_nX_{3n+1}$, (R=aromatic/alkyl moiety; B= cation; X=Cl⁻, Br⁻, I⁻). Here n is the number of the metal cation layers between those formed by the organic chains.

They are solution-processed quantum-wells (QWs) wherein the band gap can be tuned by varying the perovskite layer thickness, which modulates the effective electron-hole confinement. While the experimental interest towards this 2D class of materials is nowadays well assessed, as testified by the available literature [5], *ab-initio* studies focusing on the role of many-body effects on the electronic gap renormalization and on the nature of the optical spectra and related excitons are very limited in the 3D-OIHPs and astonishingly almost absent in the 2D-RPPs.

Accordingly, by means of a coupled GW plus BSE approach on top of DFT-KS simulations, we here study the electronic and optical properties of a 2D-RPP, *i.e.* $BA_2Pb_nI_{3n+1}$, with $n=1$ (BA=C₄H₉NH₃⁺, butylammonium), as a single sheet of atomic thickness and also as a bulk, *i.e.* a periodic QW [6]. In the nanosheet a giant band-gap renormalization of the KS band-gap is observed, while the main optical peak is due to the formation of a strongly bound almost 2D exciton. The relationship between the number of layers and the QW structure is discussed.

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#233 - Electronic and optical properties of hydrogenated Silicene on Ag(111): a computational study

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Despite the huge interest the silicene has risen as Si-based counterpart of graphene, all the extensive investigations carried onto it point to its properties being dramatically altered by the substrate onto which it is synthesized (1). Several metal surfaces have been exploited and the

Ag(111) one, which was one of the first historically considered, is no different: all studies report the loss of the desired Dirac cone due to the strength of the Si-Ag interaction affecting band structures and optical properties regardless of the specific silicene phase (2,3).

Among the several different techniques suggested to decouple the adlayer from the metal, one of the possibly simpler is the passivation through adsorption of H atoms (4). In this direction efforts have been dedicated to understand the correct adsorption configuration in the last few years (5,6). At the same time, new theoretical descriptions have been developed, tackling with good accuracy the excited states beyond the density functional theory (DFT) level (7,8). The application of these new methods to complex systems would not only provide new tools of investigation, but it would also push the understanding and the efficiency of such approaches.

In this work we theoretically investigate the adsorption of silicene-based layers onto the Ag(111) surface, focusing onto the $(2\sqrt{3} \times$

$2\sqrt{3}R30^\circ$ phase. We consider different H coverages, from the single atom to half-coverage and full coverage (so-called silicane). From a DFT description of the structural and electronic properties in the ground state, we construct the optical response and we address the features observed both in the absorption and reflectance spectra. We show the tight connection between the electronic and optical properties and, finally, the role played both by the metal substrate and H atoms.

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#234 - Excitons in MoS₂ nanoribbons: width and localization effects.

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The formation of 1D wires of carriers at the edges of MoS₂ nanoribbons (NRs) represents a case study for spontaneous polarization effects. The spatial confinement and the charge accumulation at the edges make MoS₂-NRs a perfect candidate to investigate interaction effects at the nanoscale, also in view of possible applications in solar-energy devices [1,2]. While the electronic and optical properties of MoS₂ bulk monolayers have been the focus of an intense research, the investigation of MoS₂-NRs is at the early stages. We will present a first principle investigation of the electronic structure and optical absorption of MoS₂-NRs as a function of the NR width, as obtained within the framework of many-body perturbation theory, according to the G₀W₀ plus Bethe-Salpeter-Equation scheme. We will show that both width-dependent and width-independent mechanisms emerge in the formation of excitonic excitations, and we will explain the relationship between those two mechanisms and the edge-localization of the carriers. Since the investigated MoS₂-NRs are metallic, the present work deals with the fundamental issue of the presence of excitons in metals[3].

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#235 - Hidden by graphene - towards effective screening of interface van der Waals interactions via monolayer coating

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Recent atomic force microscopy (AFM) experiments [*ACS Nano* **2014**, 8, 12410-12417] conducted on graphene-coated SiO₂ demonstrated that monolayer graphene (G) can effectively screen dispersion van der Waals (vdW) interactions deriving from the underlying substrate: despite the single-atom thickness of G, the AFM tip was almost insensitive to SiO₂, and the tip-substrate attraction was essentially determined only by G. This G vdW *opacity* has far reaching implications, encompassing stabilization of multilayer heterostructures, micromechanical phenomena or even heterogeneous catalysis. Yet, detailed experimental control and high-end applications of this phenomenon await sound physical understanding of the underlying physical mechanism. By quantum many-body analysis and ab-initio Density Functional Theory, here we address this challenge providing theoretical rationalization of the observed G vdW *opacity* for weakly interacting substrates. The non-local density response and ultra slow decay of the G vdW interaction ensure compensation between standard attractive terms and many-body repulsive contributions, enabling vdW *opacity* over a broad range of adsorption distances. vdW *opacity* appears most efficient in the low frequency limit and extends beyond London dispersion including electrostatic Debye forces. By virtue of combined theoretical/experimental validation, G hence emerges as a promising ultrathin *shield* for modulation and switching of vdW interactions at interfaces and complex nanoscale devices.

#236 - Radiation-reaction electromagnetic fields in two-dimensional crystals, a complete description of their optical properties

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A two-dimensional crystal is a macroscopic object, (even if it consists of a single plane of atoms) in the sense that a macroscopic polarization describes its interaction with an electromagnetic field. When a light wave impinge on the crystal, the observed reflected and transmitted fields are the averaged response over a region containing a significant number of atoms or molecules.

As for a three-dimensional solid, it is possible to describe a two-dimensional crystal with a microscopic atomic theory [1], regarding the material as interacting particles. Given an incident electromagnetic field, this theory computes the local electromagnetic field acting

on each atom or molecule in a two-dimensional crystal. Thus, the question that arises is how to go from the microscopic description to the macroscopic one. Surprisingly these two descriptions are connected via the radiative-reaction electric field felt by each microscopic constituent. The macroscopic electric field in the crystal is simply the incident field plus the radiative-reaction electric field [2].

The results here presented are strictly valid for single-layer two-dimensional crystals. However, the method developed paves the way to a complete treatment of the optical response of few-layer atomic crystals, hetero-structures and metasurfaces.

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Organic/Hybrid and Printed Electronics and Photonics	Stefano Toffanin
Low-dimensional Structures for Nanoelectronics and Nanophotonics	Massimiliano Cavallini
Advanced Spintronics and Nanomagnetism: Materials and Devices	Giorgio Sangiovanni
Materials and Technologies for Energy Storage	Francesca Passaretti

#237 - Organic printed electronic and hybrid printed electronic for sensing and actuation

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The continuous demands for increasing in added values, novel areas of application, reduction in environmental impact and in manufacturing costs are the major driving forces for innovation in sectors as healthcare, logistic and smart building. These challenges boosted the need for the development of alternative and more cost-effective fabrication and integration processes; organic printed electronics, when combined with state-of-the-art integration solutions, have been demonstrated to have high potentialities in this area. In this lecture some successful stories on the application of organic printed electronic and hybrid printed electronics will be presented as a way to introduce printed electronics and to highlight its potentialities. In the first part examples of the use of organic printed electronic for components development (e.g. display, sensors, actuators and energy storage units) will be presented. Finally, it will be presented how pick and place technology could be used to integrate different functional components, printed and Si-based (hybrid-printed electronic), for the development of use-and-throw systems and their application in biosensing and the safe storage and distribution of temperature sensitive goods.

#238 - Towards a flexible and biocompatible implantable sensor for wireless monitoring of human bladder volume

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The incidence of pathologies related to bladder dysfunction is clinically relevant, these including spinal injuries and neurological disorders.

A considerable part of these illnesses is associated to urinary incontinence, which is not only cause of severe discomfort for patients, but in cases of poor or erroneous treatment it could lead to infections and tissue lacerations, with serious threats for health. A number of therapies are currently available for micturition control, however a definitive solution for real-time and adequate monitoring of bladder volume is still not available. Such a solution would allow the continuous probing of the filling state of the organ, thus avoiding the insurgence of two complications, i.e. excessive expansion of the bladder and its incomplete evacuation. This aid could work in cooperation with a wearable unit or also as feedback for already existing systems apt to urinary stimulation.

We herein propose an innovative design for a capacitive strain gauge, fabricated with a hybrid process that exploits organic and flexible materials as scaffold, metallic conductive layer as electrodes and an electrical insulator coating as protective and dielectric layer. The main challenge for this application is to design a strain gauge able to match the high elasticity of the organ under study by ensuring the sensor integrity in time, as these features hardly can be found in elastomers nowadays used in biomedical implants. The original prototype introduced in this work ensures a variation of capacitance that is proportional to the bladder tissue elongation, and it is able to accommodate the wide and repeated volume changes to which the organ is subject, without exposing the device components to continuous and recurrent mechanical deformations. The proposed design allows for a discrete strain analysis exploiting a principle similar to a linear encoder, and embeds contactless communication through an integrated RF antenna. In our work, we operate the system on an artificial bladder model, demonstrating contactless data read-out via a passive communication system, and thus paving the way towards testing on more realistic *ex vivo* and *in vivo* models.

The sensing system proposed in this work thus aims at providing a novel approach to the long-standing issue of bladder volume measurements, by advancing a design that could in principle allow for easy and reliable monitoring, not achievable with current technologies. Further developments of this approach could lead to the coupling of such device to implantable stimulating ones, hence helping to restore the original bladder functionality in patients, as well as enable direct data communication and control through smartphones or other handheld devices.

#239 - Flexible and Transparent Printed Organic Field Effect Transistors and Integrated Circuits with Sub-10 V Operation

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Organic electronics is one of the key player which will enable the development of flexible and lightweight electronic circuits, in order to create portable and wearable devices with low cost and high added value. In this work, organic field effect transistors (OFETs) and circuits have been successfully manufactured onto cheap plastic substrates, by means of industrially scalable techniques.

OFETs have been fabricated in a top-gate/bottom-contact (TG/BC) configuration, with inkjet printing as the fabrication method of choice. PEDOT:PSS has been employed as conducting material, for the realization of both source and drain contacts and the gate electrode, while for the semiconducting layers poly([N,N'-bis(2-octyldecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-(2,2'-bithiophene)) (P(NDI2OD-T2)) and poly[2,5-bis(7-decylnonadecyl)pyrrolo[3,4-c]pyrrole-1,4(2 H,5 H)-dione-(E)-1,2-di(2,2'-bithiophen-5-yl)ethene] (29-DPP-TVT) have been used, as *n*- and *p*-type semiconductors respectively.

One of the main limitations of most of the state-of-the-art devices is related with their high operating voltage, which affects their stability and power consumption, hampering their diffusion in the consumer market. In order to address this issue, we employed a thin parylene-C film as dielectric layer, and successfully fabricated low voltage, transparent, flexible OFETs. The thickness of the gate dielectric layer, both with parylene alone and considering multi-layered structures, has been limited to 100 nm.

Thanks to the thin dielectric layer employed, transistors operating in the sub-10 V regime have been realized, with low leakage current density, high yield and uniform performances. The bending stability of these transistors has also been addressed, and stable performances up to 1000 bending cycles have been achieved.

The successful integration of *p*- and *n*-type devices onto the same substrate has been demonstrated, with the fabrication of well-balanced CMOS inverter logic gates, which have been integrated into more complex circuits, such as ring oscillators and D-Flip-Flops, for which correct operation has been demonstrated for voltages as low as 2 V.

The results presented in this work, exploiting scalable deposition processes, offer a viable and cost-effective path for the fabrication of all-polymer, transparent, flexible electronic devices operating at low voltages, which can easily be integrated into consumer products.

#240 - Ink-jet printing of patterned colloidal photonic crystals on PDMS substrates

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Manufacturing of three-dimensional colloidal photonic crystal patterns on soft substrates is an important topic of applied research. Here we report fabrication and characterisation of polystyrene (PS) and polymethylmethacrylate (PMMA) colloidal photonic crystal patterns on stretchable polydimethylsiloxane, PDMS films. Patterned photonic crystals on PDMS are fabricated using drop-on-demand inkjet printer. After deposition and complete evaporation of the solvent, microparticles are self-assembled into colloidal photonic crystals achieving structural colours. In order to reduce 'coffee ring' effect and to achieve high quality colloidal photonic crystal, different formulation of the colloidal inks were tested as well as PDMS films with different wettability. Surfaces of PDMS films were modified to achieve water contact angles of 90° and 60°. Using two types of solvent (water and ethanol) and three different concentrations of PS and PMMA microparticles (0.5 %wt, 2%wt and 5%wt) different colloidal inks were prepared. In order to obtain different structural colour, three different sizes of microparticles are used (diameter 211 nm, 252 nm and 262 nm). Shape and size of the droplets were analysed using optical and scanning electron microscope and structural colours were analysed using spectrophotometer, before and after stretching the PDMS films. After performed analysis colloidal ink with 2%wt microparticles where the solvent was mixture of water and ethanol (ratio 50:50) has been chosen to continue research with. Structures reported in this work have wide range of possible application in biomedical sector.

#241 - Sub-2 V MHz operation of fully solution-processed and organic field-effect transistors on plastic

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Printed and solution-processed polymer Field-Effect Transistors (FETs) hold the promise of enabling many novel applications by facilitating the accessibility of flexible, wearable and portable electronics at low-cost, owing to the suitability of the fabrication techniques and materials for high-throughput industrial production. However, the optimization of some relevant figures of merit still has to be addressed appropriately to credibly enable the implementation of many real applications. Primarily, a transistor operation frequency suitable for more demanding applications must be guaranteed (e.g. more than 10 MHz in the case of RFID-based item-tracking systems or driving circuitry for flexible displays). Secondly, the correct operation of circuits should be achieved at a bias voltage compatible with batteries or energy-harvesting devices. In addition, such goals should be conveyed through a low-cost, industrially scalable production flow.

Here, we demonstrate low-voltage, high-frequency Organic Field-Effect Transistors (OFETs) on plastic substrate exhibiting a transition frequency of 1.6 MHz at a bias voltage of 2 V and 10.4 MHz at 7 V. Such devices were realized only via the use of solution-based techniques (*i.e.* inkjet printing, bar-coating) and laser processing (femtosecond laser sintering), identifying a process flow which is suitable for the future scale-up to mass production. The high-frequency performance of the realized devices is ascribed to the combination of the high-resolution of the laser direct-writing of electrodes with the optimal charge transport properties of bar-coated poly[*N,N'*-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-(2,2'-bithiophene) (P(NDI2OD-T2)), yielding a charge mobility of 0.3 cm²/Vs (at a bias of 5 V) in devices with a channel length of 1 μm and with 1.7-μm-wide electrodes. Concurrently, the low-voltage operation was achieved thanks to a solution-processed dielectric stack integrating a low-k and a high-k material, which results in a specific capacitance of 39 nF/cm² with a gate current leakage below 10 nA/cm².

In addition, we integrated these OFETs into a rectifier circuit, which is capable of delivering a DC voltage when fed in with an oscillating input at a frequency in excess of 13.56 MHz, a standard for RFID wireless communication.

The proof of the feasibility of such low-voltage, high-frequency devices and of a rectifier capable of operating at RF frequencies, fabricated with the use of scalable solution-based techniques is a significant step forward towards the adoption of printed electronics in applications in the fields of smart tagging, wearables, large-area sensors and displays.

#242 - Large Area Printed CsPbBr₃ Nanocrystals Inks for Indoor Light Harvesting

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In less than 10 years, lead halide perovskites have gained interest for the application in a wide range of different optoelectronic fields, demonstrating impressive performances in solid-state photovoltaic devices [1] with high efficiencies exceeding 20% and great potential for lighting and lasing application [2,3]. The success of lead halide perovskites is well established thanks to the optimal optoelectronic properties. Infact, these materials show a direct gap, [4] small exciton binding energy,[5] low carrier recombination rates, [6] ambipolar transport, [7] and tunability of the bandgap range from the near infrared (NIR) [8] to the ultraviolet [9]. These materials are also very attractive for their low cost, easy processability for mass production (e.g., printing from solution) [10] and for a large availability of their chemical components.

Anyhow, to permit a real entrance to the marketing, upscaling and large area printed devices are needed and it is still one of the most ambitious challenges nowadays. In this work we investigate CsPbBr₃ nanocrystals from the synthesis to the material characterization and the device behavior. We were able to make printable inks with CsPbBr₃ nanocrystals dispersed and we make good performing standard structure solar cells with 1cm² active area. We have tested these cells under 1 sun and under 2000 Lux (2% in power of 1 sun) to exploit possible high band gap perovskite indoor light harvesting applications.

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#243 - Investigation of hybrid Josephson junctions for topological applications

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Hybrid superconductor/semiconductor devices constitute a powerful platform where intriguing topological properties can be investigated. Here we present Josephson junction devices formed by a high-mobility InAs quantum-well bridging two Nb superconducting contacts. We demonstrate supercurrent flow with transport measurements, high critical temperature of 8.1 K, and critical fields of the order of 3T. Modulation of supercurrent amplitude can be achieved by acting on two side gates lithographed close to the two-dimensional electron gas. Low-temperature measurements reveal well-developed quantum Hall plateaus, showing clean quantization of Hall conductance and demonstrating the potential of hybrid devices to investigate the coexistence of superconductivity and Quantum Hall effect.

Moreover, we present a different, fully tunable, hybrid semiconductor/superconductor device, in which the width, area, and supercurrent of the two arms of a SQUID-like geometry can be independently controlled with high precision. We show that one can tune the device from one extreme case to another: from a SQUID with narrow arms to a Fraunhofer pattern in an extended single-arm Josephson junction. Transition between these limits is investigated in a continuous manner, via electrostatic gating, without the need of additional in-plane magnetic field. Comparison between experimental results and a simple theoretical model is discussed.

#244 - Rashba spin-orbit coupling in homogeneous semiconductor nanowires

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We report k.p self-consistent calculations of quantum states in large doped nanowires (NWs) to estimate the strength of the Rashba spin-orbit coupling (SOC) in InSb and GaAs samples.

Our work relate to ongoing experiments aiming at Majorana states in condensed matter systems. In NWs, topological superconductivity can be induced by the proximity effect in the presence of both SOC and Zeeman effect. Surprisingly, very recent observations reported Rashba SOC in a wide range from 50 meVnm [1] to 270 meVnm [2] for InSb nanowire with almost identical diameter.

Our calculations for realistic NW geometries [3] include arbitrary material profiles, doping localization, and external metallic gates which break the symmetry of the NWs, giving rise to non zero SOC in low symmetry directions. We have investigated both intra-band and inter-band SOC coefficients in a broad range of NW dimensions, doping and gate configurations which allow to tune SOC to a large extent and opens to the rational design of high-SOC NW samples.

SOC results from tsymmetry and localization of the electron gas. Therefore, especially in large NWs, its intensity is determined by the complex interplay between quantum confinement, gate electric field and electron-electron interaction. Localization itself is a complex issue, since in prismatic NWs the electron gas may form both quasi-2D or quasi-1D states, mainly depending on charge density.[4] Interestingly, for high carrier densities, we have found a non-linear electric field SOC susceptibility, which abruptly switches on around zero gate voltage, and which can be traced to charge density restructuring induced by the weak electric field.

By simulating samples recently described in literature, we found good agreement with SOC observed in InSb NWs in [1], where the Rashba coupling was determined from magnetoconductance measurements using weak antilocalization theory (see the figure). Experiments reported in [2], where an extremely high SOC of 270 meVnm has been observed, could not be reproduced by our calculation, which predict values about nine times lower. We discuss the possible origin of this discrepancy. Our calculations indicate that Rashba SOC varies from 50 meVnm to 100 meVnm for typical experimental setups based on InSb nanowires for Majorana detection.

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#245 - Energy gaps of low-dimensional many-electron systems from Kohn-Sham quantities

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The electron addition energies of two-dimensional (2D) quantum dots are commonly obtained from the ground-state (gs) energies of systems with $N - 1$, N , and $N + 1$ electrons [1]. In this work we assess two alternative methods to calculate the addition energies. They resort to (a) the difference of the eigenvalues of the highest-occupied Kohn-Sham (KS) orbitals for systems with N and $N + 1$ electrons [2]; and (b) the KS gap plus the discontinuity of the exchange-correlation potential – through KS quantities for systems with N electrons

[3]. While the original definition of the addition energy involves self-consistent gs calculations for three different systems, method (a) involves two of such calculations, and method (b) only one. We analyze the performance of standard semi-local and (direct) potential approximations. We find that method (b) allows us to reduce the computational effort, yet maintaining the accuracy.

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#246 - Resistive switching and neuromorphic functionalities in ZnO Nanowires

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Memristors and resistive switching devices are among the best candidates to emulate synapses in artificial neural systems. To achieve such an ambitious goal, the intrinsic digital nature in the switching between a high and a low resistance state, typical of Resistive RAM systems, should be overcome in view of an analog behavior typical of brain synaptic strength.

In neuromorphic perspective, devices based on nanowires (NWs) could play an important role thanks to their unique characteristics. On one side, as already shown in recent years for chemical sensing and energy fields, new physical mechanisms for electrical transport can be engineered in one-dimensional nanostructures, thanks to surface and/or quantum confinement effects. On the other side, they can be employed in programmable random NW networks, a growing field of nanostructured electronic materials [1].

Here we report on the resistive switching behavior of ZnO NWs in different configurations. When Cu metalized just on the tip, we experienced an intrinsic multistate capability of polymer-coated ZnO nanowire arrays, as a consequence of charge depletion/accumulation at the nanowire surfaces, induced by electron trapping/detrapping due to redox reaction with different chemical groups present in the polymer. The experimental electrical characterizations are well supported by atomistic simulations [2]. On the contrary, when the wires are conformally coated by the electrode (both Pt or Cu), the resistive switching behavior looks dominated by a oxygen vacancies in the base layer, a thin layer of ZnO that is formed between NW arrays and the Pt substrate during the CVD growth [3].

Far better results are obtained in single NWs with Ag/Pt as electrodes, where the Ag⁺ dynamics can be fully exploited, thus obtaining in a single device most of the neuromorphic functionalities such as multistate non volatile memory, threshold switching and short term plasticity [4].

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#247 - Ionic liquid gating of InAs nanowire-based field effect transistors

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The operation of an ionic liquid-gated field effect transistor based on a single InAs nanowire will be presented and discussed. The voltage-biased ionic liquid implements the electric-double-layer inducing the field effect in the semiconductor nanostructure, and this allows to achieve the full control over the nanowire transistor. The ionic liquid gate is up to 40 times more performing with respect to the back-gate. The temperature dependence of the resistance, measured for different doping levels, reveals a clear change in the behavior of the nanostructure from fully semiconducting to quasi-metallic. Perspectives of the use of liquid gating techniques to operate nanodevices based on III-V semiconductor nanostructures will be discussed. These include fundamental and applied studies spanning from carrier density induced phase-transitions to bioelectronics.

#248 - Interface effects on the overall magnetic response of MgO/Co/MgO trilayers

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Magnetic tunnel junctions (MTJ) based on MgO tunnel barrier exhibit the highest known tunnel magnetoresistance (TMR) which can be employed in the development of sensors and data storage devices of extraordinary sensitivity. Nevertheless, experimentally realized TMR values are still an order of magnitude smaller than the theoretical predictions, and detrimental factors for TMR have not been found yet.

Processes occurring at the interface between the MgO and the magnetic electrodes are known to heavily affect the TMR and the magnetic anisotropy of the electrode. Recently, this region has attracted even more interest due to the unsolved controversy regarding the existence of a magnetic dead layer [1, 2, 3]. When Co is involved, i.e. at MgO/Co interfaces, no evidences of the dead layer are observed [4, 5]. On the other hand, recent investigations on MgO/Co/MgO trilayers show Co-O orbital hybridization, indicating CoO formation depending on the thickness of the Co and MgO layers, on the interfaces roughness, and on annealing treatments [6]. These structural modifications were found together with drastic changes in coercivity and easy axis direction, thus confirming the primary role played by the interface effects on the overall magnetic response.

In this work, we explore the buried interfaces of MgO/Co/MgO systems as a function of the Co thickness and annealing temperature, using complementary techniques such as Magneto-Optic Kerr Effect (MOKE), X-ray Magnetic Circular Dichroism (XMCD) and Soft X-ray Resonant Magnetic Reflectivity (SXRMR). Thanks to the elemental- and depth sensitivity provided by SXRMR, the chemical, structural and magnetic properties of the buried interfacial regions between MgO and Co were studied. The local magnetic moments and the direction of the easy magnetization axis were investigated as a function of depth through XMCD. Our detailed description includes thickness and roughness of each interface, oxidation states of Co, charge transfer effects at the MgO/Co interfaces, and Co oxidation/reduction processes. Furthermore, we address the thickness- and thermal- dependencies of the observed interface phenomena while accounting for the presence of a magnetic dead-layer and for the effects related to Oxygen migration/diffusion.

This complex description provides fundamental details for the understanding of how the interfacial processes affect TMR in MTJs.

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#249 - Organic spintronics: from device functionality to interfacial spin effects*Ilaria Bergenti (I) - Istituto per lo Studio dei Materiali Nanostrutturati ISMN CNR**Other Authors: Francesco Borgatti (ISMN CNR), Alberto Riminucci (ISMN CNR), Patrizio Graziosi (ISMN CNR), Mattia Benini (ISMN CNR), Alessandro Surpi (ISMN CNR) Donald MacLaren (university of Glasgow), Angelo Giglia (IOM CNR), Andrew Pratt (University of York), Valentin DediU (ISMN CNR)*

Organic semiconductors emerged as non conventional spintronic materials about ten years ago, when a few papers appeared with straightforward claims on spintronics phenomena [1]. From then on, Organic Spintronics has evolved into a multifaced discipline by a large number of theoretical and experimental investigations. One important success in the field consists in the correlation between magnetic and electronic functionalities in organic spin valves leading to memristors operating with magnetic options[2].

More recently new directions of organic spintronics became on scene: molecular materials have recently arisen as an ideal platform for creating interfacial spin effects, the so called “spinterface”[3]. Peculiar and unexpected spin and electronic properties determined by the hybridization of orbitals of molecules with the ferromagnetic surface are explored in a set of inorganic/molecular interfaces. Results indicate that the effects of hybridization extend over the first layers affecting the overall magnetic behaviour of the ferromagnet or inducing spin polarization in the non magnetic molecule over two molecular layers.

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#250 - Reconfigurable metamaterials for spin computing*Riccardo Bertacco (I) - Politecnico di Milano**Other Authors: E. Albisetti, D. Petti, S. Varotto, C. Rinaldi Dipartimento di Fisica - Politecnico di Milano*

Next generation of computing devices requires new paradigms, both on the architecture side and on the materials side. In this talk I'll present an unconventional approach based on reconfigurable magnetic metamaterials. The way they are synthesized is not the combination of different elements (as in a multilayer or in a composite material) but the crafting, at the micro- or nano-scale, of multifunctional properties in a uniform substrate. Starting from a "clean blackboard", i.e. a pre-initialized uniform film or multilayer, the use of advanced patterning techniques allows to locally modify the functional properties of said substrate in a reversible way, to define metamaterials (like in the case of photonic crystals) with intriguing peculiarities. A true engineering of the desired functionality is possible thanks to the flexibility of patterning. I'll focus on metamaterials suitable for unconventional computing strategies, all based on the use of the electron spin.

First, I'll report on a method (thermally assisted magnetic scanning probe lithography) [1] for patterning of exchange bias systems via highly localized field cooling, to define micromagnetic configurations suitable for the implementation of (i) spin wave analog computing, (ii) reprogrammable logic gates based on spin dependent transport.

Then I'll describe a strategy for patterning spin textures in ferroelectric Rashba semiconductors, such as GeTe, exploiting the intimate link between ferroelectricity and spin texture in these materials,[2] which allows for the electric writing of ferroelectric domains associated to spin-texture domains. The ferroelectric polarization provides a natural variable of state to be used for: (i) reprogrammable logic devices, (ii) neuromorphic computing.

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#251 - Co/Pd-based synthetic antiferromagnetic multi-stacks on Au/Resist underlayers: towards biomedical applications*Gaspare Varvaro - CNR, Istituto di Struttura della Materia, NM2Lab**Other Authors: Sara Laureti (nM2-Lab, Istituto di Struttura della Materia, CNR, Monterotondo Scalo (Roma), 00015, Italy) Davide Peddis (nM2-Lab, Istituto di Struttura della Materia, CNR, Monterotondo Scalo (Roma), 00015, Italy) Gianni Barucca (Università Politecnica delle Marche, Dipartimento SIMAU, Via Brecce Bianche, Ancona 60131, Italy) Annamaria Gerardino (Istituto di Fotonica e Nanotecnologie, CNR, Via Cineto Romano 42, Roma, 00156, Italy) Ennio Giovine (Istituto di Fotonica e Nanotecnologie, CNR, Via Cineto Romano 42, Roma, 00156, Italy) Denis Nissen (Institute of Physics, University of Augsburg, Universitätsstraße 1 Nord, D-86159 Augsburg, Germany) Olga Lik (Institute of Physics, University of Augsburg, Universitätsstraße 1 Nord, D-86159 Augsburg, Germany) Manfred Albrecht (Institute of Physics, University of Augsburg, Universitätsstraße 1 Nord, D-86159 Augsburg, Germany)*

Mesoscale magnetic particles are a major class of materials with the potential to revolutionize current clinical diagnostic and therapeutic techniques. They are commonly fabricated by bottom-up chemical methods; however, recent studies have demonstrated that top-down

approaches based on techniques developed for micro/nano electronics can be used to fabricate monodisperse magnetic micro/nanoparticles with a complex structure and shape that are hard to obtain by means of chemical routes [1,2]. In this work, we have exploited the possibility to use thin film stacks consisting of multiple repeats of single $[\text{Co/Pd}]_N/\text{Ru}/[\text{Co/Pd}]_N$ units with antiferromagnetic coupling and perpendicular magnetic anisotropy, as a potential starting material to fabricate free-standing synthetic antiferromagnetic microdisks. To this purpose, films were directly grown on a sacrificial resist layer spun on a thermally oxidized Si substrate, which would serve to obtain free-standing particles after its dissolution. Furthermore, the film stack is sandwiched between two Au layers to allow further bio-functionalization. The samples fulfill all the key criteria required for biomedical applications, i.e., zero remanence, zero field susceptibility at small fields and sharp switching to saturation, together with the ability to vary the total magnetic moment (by changing the number of repetitions of the multi-stack) without significantly affecting any other magnetic features. Moreover, the samples show a strong perpendicular magnetic anisotropy, which is required for applications relying on the transduction of a mechanical force through the particles under an external magnetic field, such as the mechanical cell disruption, which is nowadays considered as promising alternative to the more investigated magnetic hyperthermia approach for cancer treatment [3].

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#252 - Investigations of ferromagnet-organic bilayers for applications in spintronics

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Investigations of ferromagnet-organic bilayers for applications in spintronics

During the last decade, research in organic spintronics has clearly shown that the metal-organic interface (the so-called spinterface) plays a critical role not only in spin transport but also in modifying the electronic and magnetic properties of both the organic and the metallic side[1-3]. This is due to the formation of a “hybridization stratum” established between molecular and metallic orbitals when molecules adsorb, via chemisorption, on metallic surfaces[4].

In this work we aim to experimentally study the modification of magnetic properties, namely magnetic anisotropy, of few nanometers thin polycrystalline cobalt films upon deposition of organic molecules: C_{60} [2] and Alq_3 [3]. Since these hybridization-induced modifications only extend over few atomic layers and are critically dependent from a sharp interface, the ultra-high-vacuum MBE-based deposition procedure has been carefully tailored to ensure an extremely high uniformity and a low roughness of the cobalt layer.

Cobalt thin film morphology has been investigated by Atomic Force Microscopy showing a nanogranular structure with a medium grain size of ca. 8 nm. Longitudinal. Magneto-optical Kerr effect(L-MOKE) has been used to study magnetic properties of cobalt films. Bare cobalt thin films present uniaxial in-plane anisotropy. A distinct rotation of the magnetization easy axis of cobalt is observed upon the deposition of the organic layer, which amplitude depends on the specific molecule considered. A possible explanation involves the hybridization of the surface cobalt 3d orbitals with the molecular orbitals, leading to modifications of the electronic spin-orbit coupling and ultimately of the terms responsible for magnetic anisotropy. This work demonstrates that, at the metal-organic interface, hybridization induces measurable modifications from the physical properties of the bulk metallic component. This has possible applications in a novel beyond-CMOS technology in which all the information is completely encoded and processed within a 2D surface.

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#253 - Low temperature synthesis of L10 MPt (M = Fe, Co, Ni) nanoparticles by salt layered precursors

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Chemically ordered L1₀ magnetic alloys have attracted a great deal of attention in the last few decades due to their peculiar magnetic properties and excellent chemical stability that make them potentially suitable for various technological applications. To promote the L1₀ ordering, the processing temperature (T) needs to be higher than the kinetic ordering temperature and lower than the order-disorder thermodynamic temperature T_{O-D} . In general, the higher is T_{O-D} the larger is the magnitude of the driving force for ordering. Moreover, when sample size decreases from bulk to nanometer-scale, the optimum temperature window reduces further and for binary alloys with a low T_{O-D} the ordering cannot be achieved anymore. Therefore, lowering the kinetic ordering temperature is a critical issue being also desired for practical applications.

In this work, layered $M(H_2O)_6PtCl_6$ crystal salts ($M = Fe, Co, Ni$) consisting of alternating planes of pure M and Pt atoms were used as precursors to synthesize L1₀-MPt nanoparticles [1-3]. The ordered phase of the equi-atomic FePt and CoPt alloys is ferromagnetic at room temperature and manifests a large uniaxial magnetocrystalline anisotropy ($5 \cdot 10^6 J/m^3$ for CoPt and $7 \cdot 10^6 J/m^3$ for FePt) [4,5]. The equiatomic NiPt alloy is paramagnetic at room temperature and presents a paramagnetic-to-ferromagnetic (P-F) transition at low temperature ($< 100 K$) [6]. Using the proposed strategy, almost fully ordered FePt nanoparticles were obtained at $T = 400 \text{ }^\circ C$ and a reaction time $t = 4 h$ (order parameter $S = 0.93$, coercivity $H_c = 1.5 T$). For the CoPt alloy, a higher temperature ($600 \text{ }^\circ C$) and a longer reaction time (8 h) were necessary to obtain an almost fully ordered phase ($S = 0.93$, $H_c = 0.77 T$) due to its lower order-disorder thermodynamic temperature ($T_{O-D}-FePt = 1350 \text{ }^\circ C$, $T_{O-D}-CoPt = 825 \text{ }^\circ C$). Moreover, despite the low order-disorder temperature of the NiPt alloy ($630 \text{ }^\circ C$), partially ordered L1₀ nanoparticles ($S = 0.71$) were obtained at $T = 350 \text{ }^\circ C$ ($t = 2h$) and an almost fully ordered phase was obtained at $600 \text{ }^\circ C$ and $t = 8 h$ ($S = 0.93$); the alloy is paramagnetic at room temperature and presents Curie temperature $T_c = 80 K$ in agreement to previous studies about bulk materials [6].

In this work, we demonstrated that such a strategy allows to significantly decrease the ordering kinetic energy and consequently the temperature and/or the reaction time needed to obtain the L1₀ phase, thus paving the way for a powerful and simple method for the low-temperature synthesis of many others L1₀ binary magnetic alloys (e.g. FeNi, MnPt, FeRh, etc.).

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#254 - Ni-Mn-Ga films and nanodisks: controlling magnetism and functional properties through martensitic microstructure

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Magnetic shape memory materials show outstanding and multifunctional properties (e.g. “giant” magnetomechanical, magnetocaloric, barocaloric), originating from the occurrence of both a martensitic transformation and magnetic order. Thin films and nanostructures of these materials have a great potential for different applications, such as micro- or nano-actuators, energy harvesters, valves and solid-state microrefrigerators [1].

We have demonstrated that the microstructure and magnetic properties of Ni-Mn-Ga thin films can be engineered by properly choosing substrate, growth conditions [2] and post-growth treatments. The films have been epitaxially grown on MgO(100) or on Cr/MgO(100) by RF sputtering, with thicknesses up to 200 nm.

We have examined the relation between microstructure and magnetization process, simulating magnetization processes in films with different orientation and spatial organization of the martensitic twin variants. The micromagnetic simulations show a good agreement with the experimental results.

Starting from the films grown on Cr/MgO, we have also realized Ni-Mn-Ga nanodots ($d=160, 650 \text{ nm}$) by polystyrene-nanosphere lithography, and freestanding nanodisks, by subsequently removing the Cr underlayer via chemical etching. The microstructure and magnetic configuration of the nanostructures are influenced by the lateral confinement and release from the substrate. Furthermore, by varying temperature and applying a magnetic field to the free-standing nanodisks, we have obtained important microstructural changes, enabling different actuation modes [3].

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#255 - Alkali Clusters Intercalated Fullerides: New Materials for Hydrogen Storage

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A new class of hydrogen storage materials has taken hold in the last years: the so called alkali cluster intercalated fullerides ($A_xC_{60}, x \geq 6$) in which the fcc structure of C_{60} is intercalated by partially ionized alkali metal clusters. These materials are able to uptake high amounts of hydrogen via a reversible chemisorption mechanism at modest temperatures and dehydrogenation enthalpies ¹.

The hydrogen sorption mechanism was investigated by: 1- "in situ" neutron diffraction ² by following the evolution of the structure on increasing the temperature under hydrogen pressure and 2- muon spin rotation spectroscopy ³ thanks to the capability of this technique to follow the muonium reactions (a muon-electron bound state similar to an hydrogen atom).

The evolution of the structure under hydrogen pressure on increasing temperature shows that in the case of $x=6$ the hydrogenation of C_{60} is the first process to occur, eventually associated with a fcc to bcc structural phase transition. At moderate degree of C_{60} hydrogenation, a segregation of LiH is observed which progressively reduces the nuclearity of the intercalated clusters. This process decreases the efficiency of the cluster mediated hydrogen molecule dissociation, thus leading to the end of the absorption process occurring around 350C.

During the desorption both processes (hydride formation and fullerene hydrogenation) reverse and the original material is fully restored.

Implanted muons can also probe the chemisorption process through the formation of muonium, which is an isotope of hydrogen. The observed formation of a muon adduct radical confirms that C_{60} hydrogenation is the first process to occur, but its efficiency, related to the amplitude of the radical signal, increases on lowering the temperature down to 5K. This indicates that the cluster mediated hydrogen dissociation is the process requiring the relatively high temperature needed for the storage process.

In conclusion, the combination of in-situ neutron diffraction and muon spectroscopy allowed to disclose the hydrogenation mechanism of these new type of hydrogen storage materials. The results obtained give suggestions on how to further improve the (already satisfying) performance of these systems.

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#256 - Graphene foam composites for high performance Li ion batteries

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Ultra-light 3D graphene structures called graphene foams may be produced top-down via chemical exfoliation methods,[1] but they suffer from relatively poor electrical conductivity due to oxidation defects and poor mechanical robustness. Alternatively, high quality graphene foams with very high conductivity may be produced bottom-up via Chemical Vapour Deposition.[2] These unique structures have been investigated for a wide range of applications, such as electrodes in batteries and supercapacitors, biological scaffolds, sensing, and many others.

We describe our research into using these graphene foams in supercapacitors and batteries. Alone, the capacitance of the foams is very low, but it may be significantly improved by the addition of a coating of metal oxide nanoparticles such as Fe_2O_3 . We developed and optimised an electrochemical procedure for the deposition of Fe_2O_3 nanowalls uniformly across the whole structure. In this way, we could reach a capacity of over 300 F/g. However, the capacity significantly decreased over extended cycling due to detachment of and damage to the metal oxide layer. To overcome this problem, we added a protective layer of electrochemically-exfoliated graphene oxide (EGO), which successfully stabilised the structure during cycling. Using this technique, it will be possible to produce optimised graphene foam composites with very high capacities and even hybrid structures using other metal oxides. In addition, we were able to further increase the areal capacity of the composites by using EGO as a spacer for adding more layers of oxide nanoparticles.

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#257 - Reduction Properties of (001) Maghemite Surfaces

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Metal oxides have attracted more and more attention during the last years as materials suitable for applications in catalysis and are therefore objects of a search for new materials with an higher catalytic activity, and more suitable for green processes [1]. The research of new efficient catalysts is crucial in many industrial processes. In particular, Iron Oxides have been demonstrated to be good catalysts, and recently it has been asserted that the (001) maghemite ($\gamma\text{-Fe}_2\text{O}_3$) surface may have an high catalytic activity. Oxygen reduction plays a crucial role in the electro-chemical energy storage and conversion as in metal-air batteries or in fuel cells [2]. Qui et al. [3] have shown experimentally that maghemite shows a great promise for oxygen reduction reactions, and could be a good candidate for cost effective catalysts. The reduction of the surface, furthermore, could affect the catalytic activity of the CO oxidation reaction considering it could follow the Mars Van Krevelen mechanism. Maghemite is the second most stable polymorph of iron oxides: it is obtained by magnetite (Fe_3O_4) but it has been much less studied. Maghemite, like magnetite, has a spinel crystal structure, however, to guarantee the neutrality of the structure, since all the octahedral and tetrahedral iron atoms of the bulk are in a trivalent state, the presence of cation vacancies is required in the unit cell. Due to the intricacy of the bulk structure, to our knowledge, this is the first ab-initio study concerning the reduction properties of the (001) maghemite surfaces where the iron vacancies are taken explicitly into account. All the calculations have been performed in a density functional approach (DFT) as implemented in the Quantum Espresso (QE) code [4],[5]. In order to describe in a right way the electronic properties of the oxide, it is required the use of the Hubbard correction (DFT+U). All the calculations are spin polarized, and the surfaces were modelled with the slab method. We have calculated the formation energies of Oxygen vacancies on two different (001) surface terminations, both iron and oxygen terminated, characterized by a different location of iron vacancies. We have correlated the formation energy with the Oxygen atom positions. Besides, we have found that maghemite surfaces are more reducible than magnetite one: this is due to the presence of the iron vacancies. Indeed, the formation energy is related to the charge transfer in iron atoms, which is different for the two oxides. The creation of the oxygen vacancy, furthermore, causes a variation of the magnetic and electronic properties of the two different maghemite surfaces terminations.

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#258 - High-capacity Si-based nanocomposite anodes for Li-ion batteries

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The massive development of Li-ion technology has fostered the spread of electrical vehicles (EV) with higher driving range. However, the ever-increasing demand in energy density requests for a breakthrough in Li-storage materials. High-capacity anode materials, alternative to the commonly used graphite, have been investigated for several years. Among these, Si plays a special role because of its extremely high theoretical capacity (up to 4200 mAh g^{-1}), which is however associated by severe volume changes (up to 300%) due to Li alloying/dealloying processes, representing a severe limitation to the electrode and cell reversibility and durability.

In this context, the electrochemical behaviour of several nanocomposite materials, based on commercial Si powder of about 100 nm size in which the volume changes are buffered by organic or inorganic matrixes, such as graphene or transition metal oxides, is here presented. The electrodes and cells performances, in terms of specific capacity and durability, are enhanced by optimized electrode and electrolyte formulations, at the same time paying attention to cost and sustainability. A rationale of the improved behaviour is explored by applying several morphological, structural and electrochemical investigation techniques, with a special focus on electrode/electrolyte interfacial properties.

#259 - NUCLEATION AND GROWTH OF ZIF8 THIN FILMS ON SILICON-BASED SUBSTRATES

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Metal Organic Frameworks (MOFs) have become increasingly promising materials for a wide range of technologies because of their high surface area, versatility, and chemical stability. MOFs are hybrid porous complexes in which periodic arrangements of metal clusters are connected by organic ligands. Among all possible MOFs topologies, ZIF8 that consists of $Zn(MeIm)_2$ (HMeIm: 2-methylimidazolate), has great potentialities for gas and energy storage, chemical sensing and nanodevices. Several synthesis methods based on direct approaches, like solvothermal or microwave-based and electrochemical protocols, and on layer by layer deposition (LBL) carried out by employing OH or NH_2 -terminated surfaces, have been proposed to obtain ZIF8 film. Here, through direct synthesis and by changing the solvent, it has been studied the role of surface chemistry on ZIF8 film growth. Si (100), Quartz, amorphous Si (a:Si) and silicon with native oxide have been employed as surfaces. The film preparation was carried out through sequential one-pot method, without additive, at room temperature and using a mixed Zn nitrate and imidazole solution either in MeOH or EtOH. Films were characterized by ellipsometry, XRD, SEM and XPS. Using MeOH a solvent, fast ZIF8 nucleation was observed both in solution and on the surface leading to powders and thick films. Well-grown films were, hence, obtained on quartz, a:Si and Si(100), while a poor coating was formed on SiO_2 . From ethanol solution, slower grow rates occurred, so that the crystal formation in solution was negligible and thinner films compared with the ones in MeOH were deposited. The lower polarity of ethanol slows down the homogenous nucleation and allows to detect the substrate effect. The different surface reactivity towards ZIF8 functionalization is attributable to the diverse silanol densities on the various surface and, in turn, to the different Lewis basic strength which can accelerate imidazole deprotonation. Si(100), being the surface with lower silanols density and exhibiting more basic behaviour, promotes the imidazole deprotonation, key step of ZIF8 formation. Indeed, Si results the most reactive surface towards ZIF8 functionalization and the growth rates on the diverse substrates increases according to the following order $SiO_2 < quartz < amorphous Si < H$ -terminated Si. On this background, ZIF8 film has been grown on copper foils that being characterized by a heterogenous surface with a thin oxide layer onto it, promotes either, the homogenous both heterogenous nucleation obtaining thick ZIF8 films. ZIF8 coating copper foils have been tested as anode for lithium ion battery and have been doped, furthermore, with lithium salts to obtain Li^+ conductors.

#260 - Electrochemical intercalation of fullerene and hydrofullerene with sodium

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INTRODUCTION

Li-ion batteries (LIBs) are currently the most widespread rechargeable power sources employed in various portable devices, but one of their main drawbacks is represented by the relative scarcity of lithium in the Earth's crust, preventing their large scale implementation, especially in the automotive field¹. The replacement of lithium with sodium offers an alternative strategy, since sodium is largely available in nature². However, typical anode insertion materials for LIBs, such as silicon and graphite, do not work in sodium-ion batteries (SIBs)². In this work we demonstrate the ability of fullerene C_{60} and hydrogenated fullerene $C_{60}H_x$ ($x \sim 39$) to operate as negative electrodes in novel Na-ion batteries³.

EXPERIMENTAL

Electrochemical and structural properties of the fullerene electrodes were investigated through cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) of the electrodes, impedance spectroscopy and powder X-ray diffraction.

RESULTS AND DISCUSSION

CV performed on the half-cells confirmed the availability of up to six reversible red-ox states for C_{60} , accordingly to literature, and up to four reversible red-ox states for $C_{60}H_x$ ³. GCD measurements indicated specific capacities after the first cycle of 250 mAh g^{-1} and 230 mAh g^{-1} for C_{60} and $C_{60}H_x$ respectively³. Building upon the known solubility of C_{60} in common organic electrolytes used in batteries, we developed a suitably optimized solid-state Na-(polyethylene oxide) electrolyte for this application³.

CONCLUSION

Both C_{60} and hydrogenated C_{60} have been electrochemically intercalated with sodium. However, C_{60} electrode shows a strong irreversible character after the first discharge. On the contrary, $C_{60}H_x$ displays better reversibility, suggesting that hydrogenation of the buckyball could be effective to preserve sufficiently large interstitial pathways for Na^+ diffusion upon intercalation³.

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#261 - Investigation of Li and Na dynamics in $\text{Na}_x\text{Li}_{6-x}\text{C}_{60}$

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Lithium and sodium cluster-intercalated fullerides (A_xC_{60} ; A = Li, Na and $x = 6, 12$) display good performances as hydrogen absorbing materials or as potential components in ion batteries. Li and Na ions, thanks to their small ionic radius, are easily intercalated in the interstices of the fullerite lattice with two tetrahedral and one octahedral sites per C_{60} molecule, which favor the formation of small alkali clusters.

Light alkali and alkali earth (Li, Na, Mg) intercalated fullerides have been received great attention in the recent past, thanks to the ability of the metal ions to diffuse among the C_{60} lattice interstices already at low temperature, thus displaying fast ion conductivity [1].

Here we report on the Na, and Li dynamics in $\text{Na}_x\text{Li}_{6-x}\text{C}_{60}$ fullerides ($x = 0, 1, 5$, and 6) in the temperature range 80–550 K by using ^{13}C , ^{23}Na , and ^7Li solid state NMR [2,3]. The results show that the C_{60} reorientation dynamics is hindered at room temperature for the Li-enriched fullerides, but it is active for the Na rich ones with a rate of the order of few kilohertz.

^{23}Na and ^7Li NMR measurements show the presence of two dominant thermally activated dynamics that can be associated with Li/Na ionic motions within the octahedral sites (intrasite motion) and between the octahedral and tetrahedral sites (intersite motion).

We show that the substitution of one Na or one Li ion in the end members Li_6C_{60} and Na_6C_{60} , respectively, yields to an increase of the hopping rate of the intersite motion, which is necessary for the ionic diffusion in possible fulleride-based ionic conductors.

These results will be compared also to the Li and H dynamics recently studied [4] in $\text{Li}_{12}\text{C}_{60}$ and $\text{Li}_{12}\text{C}_{60}\text{H}_y$, investigated by means of ^7Li and ^1H solid state Nuclear Magnetic Resonance.

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#P001 - Small size thermoelectric power supply for battery backup*Hossein Abedi - CNR-ICMATE*

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In the past years, a lot of works have been reported on thermoelectric generators (TEGs) as power supplies and as alternative technology [1-3]. In this work, a TEG based on a catalytic combustor fed with propane/air mixture has been developed having as target output and size the one proper of AA batteries. Catalytic combustion is particularly appealing for thermoelectric conversion due to its high power density coupled to the relatively low burning temperature.

The electrical output and size of the largely used AA batteries, together with catalytic TEG benefits such as reliability in continuous operating conditions, fast source recharging and adaptability are strategic features opening interesting opportunities for thermoelectric technology applications.

The system has been electrically characterized in different ranges of fuel flow rates at constant power and constant temperature conditions. The different contributions to the overall generated power have been identified through the balance of power in/out at the maximum power production condition. TEG efficiencies and thermal resistances have been evaluated by performing high quality temperature and power characterization. Besides, using FT-IR analysis for exhaust gas composition measurements, the chemical efficiency has been obtained. Finally, a discussion on output and thermal circuit suitability of the TEG has been presented.

With the present TEG system an output up to 4.3 W (4.65 V, 0.93 A) has been achieved by using a fuel consumption of 4.1 g/hr, typical of in battery side technology. Moreover, the maximum overall efficiency of 3.4% has been obtained with an effective thermal design.

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#P002 - Mucoadhesive Solid Lipid Microparticles (SLMs) for controlled release of docosahexaenoic acid (DHA)*Erika Amore - Istituto per lo Studio dei Materiali Nanostrutturati (ISMN), U.O.S. Palermo, CNR.*

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In the last few years there has been a considerable interest in food and beverage product containing polyunsaturated fatty acid (PUFAs), and in particular omega-3 (ω -3) fatty acids, because of their potential health benefits. Indeed, it has been observed that consumption of significant amounts of ω -3 fatty acids is associated to a reduced risk of several types of chronic disease, including inflammation, cardiovascular disease and immune response disorders.

The three most common ω -3 fatty acids are: α -linoleic acid (ALA, 18:3), eicosapentaenoic acid (EPA, 20:5) and docosahexaenoic acid (DHA, 22:6). These molecules show very low water solubility and high susceptibility to degradation through oxidation, which results in generation of rancid and potentially toxic products. A combination of different strategies can be used to control lipid oxidation and to achieve a long shelf life. In particular, the encapsulation of these lipophilic nutraceuticals into targeted drug delivery systems can prevent physical or chemical degradation mechanisms.

In this work we describe the preparation and the characterization of Mucoadhesive Solid Lipid microparticles (SLMs) for controlled release of DHA. The obtained systems have been characterized in terms of size, zeta potential, mucoadhesive properties, loading capacity (LC) and release properties. The mucoadhesiveness of microparticles prepared represents a good strategy to potentially improve the retention time of the drug at the site of application, pharmacokinetics and so the efficacy of drugs delivered by topical route (Amore et al. Nanomed. 2017, 12(19), 2287).

The release studies of SLMs containing DHA showed an initial burst release of about 30% of drug and subsequently, a prolonged release up to 72h, with only 50% of drug released after this time. Moreover, the percentage of drug not yet released was found all inside the microparticles, so this amount could be available after this time.

These preliminary results suggest that the SLMs here reported could be potential carriers for the targeted delivery of DHA.

#P003 - Statistical inference for image reconstruction through multimode fibers*Daniele Ancora - CNR-NANOTEC*

One of the biggest challenge in the field of biomedical imaging is the comprehension and the exploitation of the photon scattering through disordered media: Many studies have pursued the solution of this riddle achieving light-focusing control or for reconstructing images in complex media. In the present work, we investigate how statistical inference could help the calculation of the transmission matrix in a multimode fiber, thus enabling its usage as a normal optical element. Our desired goal is to uncover insights from the scattering problem, encouraging the development of novel imaging techniques for better medical investigations.

#P004 - Creep characterization of a nickel-based superalloy for sCO₂ turbomachinery for green power generation*Giuliano Angella - CNR-ICMATE*

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Thermodynamic cycles using CO₂ in supercritical conditions (sCO₂) can provide many advantages for future power generation applications. Thanks to the high fluid density, sCO₂ causes a significant machinery size reduction, along with the possibility to achieve very good efficiencies. Due to thermal stability and non-flammability of sCO₂, direct heat exchange from a wide range of thermal sources is possible from relatively low to very high temperatures. This makes sCO₂ suitable for micro-channel-based heat exchanger technology in close-loop systems in combination with thermal solar power (CSP), biomass, flaring, nuclear and even geothermal sources. However, with sCO₂ material selection and design problems can raise, since materials must have resistance to [high-temperature oxidation](#), corrosion and deformation under constant mechanical loading ([creep](#) resistance), so nickel-based superalloys for turbo-machinery components, and [austenitic and ferritic stainless steels](#) for piping should be used in sCO₂ cycles.

Exergy S.p.A. is focused to develop a new turbo-machinery for sCO₂ in close-loop systems for direct heat exchange from green thermal sources, and in ICMATE Milan the nickel-base superalloy A286 that is widely used in aerospace applications, has been investigated through simulating the operational conditions of temperatures (560-720°C) and mechanical loadings (200-560 MPa) typical of sCO₂ close-loop systems in order to test the alloy feasibility to be used in turbo-machinery components like shafts. Different production routes were also imposed to A286 by changing heat treatments and deformation conditions prior creep testing to find the optimal response of the alloy to the operational conditions. Results concerning the mechanical response and the microstructure evolution of A286 under creep conditions are reported.

#P005 - Data-Matrix technology for quantitative Multiparameter Monitoring of Cell Cultures*Marianna Barbalinardo - CNR-ISMN*

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Cells can be used as efficient sensors exploiting their change upon external/internal stimuli morphology, shape, immunofluorescence and so on. Moreover, cell cultures are one of the most powerful activity for the initial stage of a variety of application in life science, ranging from the mono-cellular level study to complex multicellular tissue and regenerative medicine. The number of cells adhered on a substrate, their morphology, spatial distribution and the capacity to migrate are widely used information to establish cell wellness and as a first order characterization the differentiation stage. We developed a new method, in which we addressed the problem of multiparameter monitoring of cell cultures by introducing the data-matrix technology in cell biology as an efficient method for facile, real time, multi-parameter monitoring of cell cultures. The method exploits the know-how developed for error handling in digital information technology developed for satellite communications and used for data-matrix technology. The method is based on the measure of reading errors induced by intervening cells upon checking a fluorescent data-matrix code placed behind them. By reading fluorescence images via a modified data-matrix reader of a smart-phone, the method delivers number of fluorescent cells, coverage and time evolution. The process has been demonstrated with several immunostained model cell cultures as well as by monitoring the evolution in time of green fluorescent protein in a fibroblast culture and for cell sorting.

#P006 - Thermal kinetic of TPA⁺ release and structural changes of ZSM-5 combining an "in situ" time-resolved synchrotron powder diffraction study and ex-situ thermal analysis*Giada Beltrami - University of Ferrara*

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The study of the zeolite behaviour upon heating and their consequent structural modifications is of particular importance since catalytic properties, molecular sieve effects are remarkably enhanced in the dehydrated/calcined state and at relatively high temperature. The structural modifications occurring in the zeolite framework are affected by several intrinsic chemical and structural factors (*i.e.*, framework topology, Si/Al ratio, charge-compensating cations, coordination of bare cations, crystal size, heating rate, etc.) [1-3]. In this work, the structural modifications of a ZSM-5 zeolite with Si/Al ratio (SAR) of 51, as a consequence of the degradation of the template, tetrapropylammonium ion (TPA⁺) and the release of water molecules upon heating, in the range between 25 and 800 °C, has been studied combining an *in situ* synchrotron radiation powder diffraction and ex-situ thermogravimetric analysis. The time-resolved experiment, performed at the MCX beamline at Elettra allowed to monitor through structure Rietveld refinements the evolution of the lattice parameters and the occupancy variation of the TPA⁺ and water molecules up to 800 °C. High temperature experiments confirm that the ZSM-5 maintains its crystallinity and its symmetry (*i.e.*, orthorhombic, *s.g.* *Pnma*) within the investigated T-range. In particular the inspection of the Fourier map at Room Temperature, located the TPA⁺ at the intersection of the straight and sinusoidal channel, according to the literature [4]. The analysis of bonding distances has shown that the template does not interact with the framework oxygens, but only with the water molecules, also located in the intersection of the channels, through hydrogen bonds. The *in situ* and ex situ techniques showed a similar total weight loss (14 and 15 %, respectively), but indicated a different temperature and kinetics of TPA⁺ and water release (400 and 510 °C, respectively). Specifically, the cell parameters constantly increase with the temperature up to 200 °C, as a consequence of the increase of the CFA and the partial disordering of the water molecules inside the channels. After 200 °C, when the template degradation and water molecules desorption begin, the thermal expansion becomes negative.

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#P007 - Tuning polymorphism in 2,3-thienoimide capped oligothiophene based field-effect transistors by implementing vacuum and solution deposition methods

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We investigated the impact of the molecular packing and film morphology on the field-effect charge mobility in 2,3-thienoimide-based oligothiophenes semiconductors (Cn-NT4N). Organic field-effect transistors were realized by implementing both vacuum and solution methods in order to control the solid-state phase of the active layer. Indeed, controlling the polymorphism of the active layer is an effective strategy for tuning the electrical properties in organic devices. Thermal sublimation in high vacuum chamber and Supersonic Molecular Beam Deposition were used as vacuum-based fabrication approaches while Lithographically Controlled Wetting was used as a solution-deposition technique. Thermal sublimation led to thin-films with a phase packing showing ambipolar behaviour. By tuning the deposition rate, Supersonic Molecular Beam Deposition enabled the formation of two crystal phases showing different electrical behaviour. On the other hand, Lithographically Controlled Wetting allowed the formation of Cn-NT4N microstructured active layers and their implementation in field-effect transistors.

#P008 - Additive Manufacturing of ceramic materials with Filament Extrusion 3D Printing

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Additive manufacturing (AM) is a technology having great potential for the development of sustainable process to produce near-net-shape components. The addition of material, instead of its removal, reduces waste, machining operations, production time of prototypes and allow component design not obtainable with traditional manufacturing processes. Since about three decades, AM technologies have been used for processing of polymeric or metallic materials, in order to fabricate prototypes or models, and new products are now on the market. Similar results are expected from AM of technical ceramics, but ceramic processing is difficult due to the more demanding parameters to obtain the final component: the consolidation requires high temperature sintering and the feedstocks are not easy available on the market. In the Filament Extrusion 3D Printing of ceramics, the feedstock is a paste, with an extrudable composition where the high solid content promote the green density. A crucial stage is the setup of the paste, in order to produce a final object with

the desired physical characteristics. The preparation of the paste as feedstock implies the optimization of the rheological behaviour during extrusion stage that is achieved by the control of several factors as: particle size distribution of the ceramic powders, content and type of rheological additives and solvents, control of the pH and the mixing technique. Furthermore, once the green object was printed, one or more treatments are needed for debinding and sintering, where the removal of organic additives and the consolidation of the material lead to the final object; the shrinkage of material occurs during thermal treatments and the parameters are finalized to avoid crack formation, obtain a specific microstructure and reduce production time: for example to promote density, when the porosity is an undesirable defect contributing to the failure of the system, or to obtain a controlled porosity with tailored pore structures for special applications.

Studies on the feasibility of printing ceramic materials have been conducted for both oxide and non oxide based materials, aiming at demonstrating the versatility and potential of the Filament Extrusion 3D Printing in several application. Technical ceramic objects, with relative simple geometry, were realized starting from the experimental optimization of the slurry up to the material sintering.

#P009 - Illuminating Correlative Battery Research using Light, X-ray and Electron Microscopy

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X-ray tomography has emerged as a new powerful imaging technique that obtains 3D structural information from opaque samples under a variety of conditions and environments. It has rapidly become an accepted laboratory technique offering quantitative information in materials science. With batteries application examples, we present ways in which non-destructive 3D volumetric information, obtained via laboratory nanoscale and sub-micron X-ray microscopy (XRM) are increasingly used to probe scientific questions as a complement to Electron- and Light-based microscopy methods. These correlative methods, relating to XRM, provide an opportunity to study materials evolution at multiple length scales in 3D and utilize this information to inform or guide postmortem analysis to be most efficient.

#P010 - Preparation of graphene-based films with tuned structural and electrical properties

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Graphene-related materials (GRMs) comprise structurally complex membranes, incorporating topological defects (i.e. non-hexagonal rings, vacancies, grain boundaries), as well as a large amount of functional groups (i.e. hydroxyl, carboxyl, epoxide,...). This is a result of a chemical synthesis using exfoliation of graphite through acid treatments and chemical reduction processes. The possibility to produce large quantities of GRMs with controlled characteristics is highly relevant for applications in composites, energy storage, and sensing [1], but demand a careful optimization of their properties which presently lack guiding rules.

We focus on solution processing to produce large amounts of GRMs in stable suspension, exfoliating commercial graphite powder (Sigma Aldrich, 99% pure, <150 µm) via chemical- (GO) [2] and electrochemical- (e-GO) [3] approaches.

Exploiting the high processability (stable in water and in most of the common organic solvents) and the chemical tunability of such materials, we fabricate macroscopic films by vacuum filtration with controlled thickness (between 200 and 400 nm) and oxygen content (from 50% to less than 2%, in weight).

We use a multi-scale approach to characterize the fabricated materials, from solutions to final films. We perform quantitative measurements to correlate the morphology of single GRMs, as deposited by solution on ultra-flat surface, with the chemical composition and the electrical properties of the film, developing reliable protocols exploiting Atomic Force Microscopy (AFM), X-ray Photoelectron Spectroscopy (XPS) and 4-point probe analysis.

A reliable quantitative characterization is a fundamental requirement in order to optimize the materials properties, paving the way to large-scale production of GRMs with pre-programmed functionalities.

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#P011 - Influence of Extreme Ultraviolet irradiation on structural properties of CVD grown graphene studied by Raman mapping, SEM and AFM.

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Creation of defects in graphene alters its properties providing a way for engineering its functionality. A key challenge of this area of graphene research is the ability to induce defects only within the specific area of interest and then be able to image the obtained structure without creating other defects. One of the methods for modifying the properties of carbon materials with controllable spatial precision is the formation of defects through Extreme Ultra- Violet (EUV) irradiation.

In this work, we report micro-Raman, SEM and AFM investigations of changes in the single graphene crystal lattice induced by EUV irradiation. CVD grown mono-layer graphene films (Graphenea) were irradiated at four different doses by using the ENEA Discharge Produced Plasma (DPP) EUV source. The DPP emits more than 30 mJ/sr/ pulse on the 10-18 nm wavelength band (69-124 eV).

It was found that the under EUV exposure defects as bubbles, cracks and holes only in the irradiated areas. These defects were generated in the carbon matrix due to the breaking of sp^2 bonds with a subsequent graphene doping in the DPP vacuum chamber residual atmosphere.

#P012 - Microbial Synthesis of Chalcogen and Metal Nanoparticles by Phototrophically grown *Rhodobacter Capsulatus*

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We describe how the photosynthetic bacterium *Rhodobacter Capsulatus* (RC) can be employed for the biosynthesis of Te(0), Se(0) and Zn(0) nanoparticles (NPs) in aqueous solution at room temperature. Resulting NPs are highly crystalline, resistant to flocculation for weeks after purification, and their average size can be tuned by varying incubation time. NPs with mixed compositions can also be obtained with the same process.

The intake of chalcogenide and metal oxyanions by RC normally results in the formation of intracellular deposits after their reduction in the cytoplasm, as in other bacterial species. However, catalytic amounts of the redox mediator lawsone (2-hydroxy-1,4-naphthoquinone) induce an abundant formation of NPs outside cells^{1,2}. Resulting NPs have a polycrystalline core coated with biopolymeric material which proves to be highly functional to their stability in solution. We report on the main incubation parameters influencing NP biosynthesis, and characterize products via AFM, HR-TEM, EDX microanalysis, UV-Vis spectroscopy, SDS-PAGE, FTIR, DLS and MALDI-TOF MS.

We also discuss how the procedures described above could be applied to bioremediation and biorecovery of chalcogens and transition metals from contaminated wastewaters.

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#P013 - Silica shell on Gold Nanorods: a tuneable, protective and versatile coating

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Silica is a fascinating material for its versatility and modularity; gold nanoparticles coated with it can be useful in various fields from metamaterials to several biotechnology applications. (1)

In this light, our group is working on the preparation of CTAB-coated gold nanorods (AuNR@CTAB) covered with silica (AuNR@SiO₂). We tuned the silica thickness by modulating the ratio between AuNR@CTAB to TEOS concentration obtaining AuNR@SiO₂ with thickness varying from 3.5 to 30 nm. Playing with the thickness of the silica coating is a way to change the optical properties of gold nanorods.

On this perspective, using the silica shell thickness as spacer, we estimated the distance between nanoparticles necessary for the plasmon interaction. By measuring the edge-to-edge distance between the gold core, in fact, we found that it shortens by decreasing the silica thickness, so allowing a better coupling. Furthermore, by heat treatment, we are trying to control the silica porosity as a new challenge for modulating the plasmonic field.

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#P014 - X-ray fluorescence spectrometry beamline at Elettra Sincrotrone Trieste. Perspectives for trace element analysis in material science and environmental applications

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The X-Ray Fluorescence (XRF) beamline, operated by Elettra Sincrotrone Trieste and the International Atomic Energy Agency, hosts an end-station devoted to X-ray emission and absorption spectrometry under ultra-high vacuum conditions [1-2]. Thanks to a double crystal monochromator, the X-ray beam can be tuned in the energy range from 3.6 to 14 keV. A motorized sample manipulator coupled with additional motorized stages can move both the sample and the detectors with respect to the beam, setting up several excitation/detection geometries. In addition to the conventional reflection geometry (XRF 45/45), angle-dependent experiments like Total external reflection X-Ray Fluorescence (TXRF), Grazing Incidence/Exit X-Ray Fluorescence (GI/GE-XRF), and X-Ray Reflectometry (XRR) can be performed. The advanced sample manipulation system can also be exploited to combine different experimental strategies at the same time: this can be the case of simultaneous GIXRF and XRR scans for the study of nano-layers, or X-ray Absorption Near Edge Spectrometry (XANES) carried out in TXRF geometry for the analysis of trace elements speciation.

The information accessible with the abovementioned techniques is of interest for a wide variety of fields. The majority of the beamtime allocated for external users is employed for the environmental studies, mostly focussing on air or water pollutants in different areas of the world [3-6]. Nevertheless, XRF is well suited for other kinds of science, including medicine [7] and life science, e.g. to study the diseases related to the development of human civilisation [8]. The facility is also used to address issues related to basic physics and material science domains [9], especially through the enrichment of existing databases with newest evaluations of fundamental parameters for the interaction between X-rays and matter [10-12].

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#P015 - MD-FEM Force Field Simulations of Particle Subjected to Dielectrophoresis Interactions

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Particles with sizes that range from sub-micrometers to about 1 millimeter and with particular electrical and/or magnetic properties, experience mechanical forces and torques when they are subjected to electromagnetic

elds (this type of particles are called "electromechanical particles"). The theoretical study of this large class of complex systems is possible thanks to the development of real-system models and numerical simulations of the stable (multi-particle) con

gurations and their dynamics. One of the phenomena that affect electromechanical particles is the dielectrophoresis (DEP). A branch of emerging application relates to controlled manipulation of particles dispersed in colloidal solutions (i.e. biological particles such as cells or DNA), since the strong selectivity of the response depends on the particle volume, shape and composition. Application

elds of dielectrophoresis include cell partitioning/isolation for the capture/separations without the use of biomarkers. This contribution focuses on the theoretical study of the dynamics of micro-sized spherical biological particles suspended in a colloidal solution, which are subjected to dielectrophoresis in the presence of non-homogeneous and non-uniform variable electric

fields. The electric

field is applied through the electrodes present in a microfluidic channel in which the colloidal solution flows. In this work, we present numerical simulations of the movement of MDA-MB-231 tumor cells near electrodes edges; we run a more detailed study, with a non-approximate calculation of the dielectrophoretic force: DEP forces are estimated by integrating the Maxwell Stress Tensor. The dynamics is simulated by techniques borrowed from Molecular Dynamics (MD): our goal is to fi

rst evaluate the forces acting on electromechanical particles starting from the initial con

guration of the system and then calculate the dynamics of the particles through the integration of the equations of motion using MD-like techniques. The coupled MD-FEM algorithm and its implementation in the FEniCS environment are presented. Realistic simulated cases will be discussed. We carry out simulations of the movement of MDA-MB-231 tumor cells and B-Lymphocytes near the electrode edges. Our work shows the potential of coupled MD-FEM study of electromechanical particles.

#P016 - MD-FEM Force Field Simulations of Particle Subjected to Dielectrophoresis Interactions

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Particles with sizes that range from sub-micrometers to about 1 millimeter and with particular electrical and/or magnetic properties, experience mechanical forces and torques when they are subjected to electromagnetic fields (this type of particles are called "electromechanical particles"). The theoretical study of this large class of complex systems is possible thanks to the development of real-system models and numerical simulations of the stable (multi-particle) configurations and their dynamics. One of the phenomena that affect electromechanical particles is the dielectrophoresis (DEP). A branch of emerging application relates to controlled manipulation of particles dispersed in colloidal solutions (i.e. biological particles such as cells or DNA), since the strong selectivity of the response depends on the particle volume, shape and composition. Application fields of dielectrophoresis include cell partitioning/isolation for the capture/separations without the use of biomarkers. This contribution focuses on the theoretical study of the dynamics of micro-sized spherical biological particles suspended in a colloidal solution, which are subjected to dielectrophoresis in the presence of non-homogeneous and non-uniform variable electric fields applied through the electrodes present in a microfluidic channel in which the colloidal solution flows. In this work, we present numerical simulations of the movement of MDA-MB-231 tumor cells and B-Lymphocytes near electrodes edges; we run a detailed study, with a non-approximate calculation of the dielectrophoretic force: DEP forces are estimated by integrating the Maxwell Tensor. The dynamics is simulated by techniques borrowed from Molecular Dynamics (MD): our goal is to first evaluate the forces acting on electromechanical particles starting from the initial configuration of the system (position of the particles, geometry of the electrodes, electrical potentials applied), and then calculate the dynamics of the particles through the integration of the equations of motion using MD-like techniques. The coupled MD-FEM algorithm and its implementation in the FEniCS environment are presented. Realistic simulated cases will be discussed. Our work shows the potential of coupled MD-FEM study of electromechanical particles.

#P017 - MOCVD grown, fast switching phase change In-doped Sb nanowires

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In-doped Sb nanowires (NWs) with diameters down of (20 – 40) nm were grown by Metalorganic Chemical Vapor Deposition (MOCVD) via the vapor-liquid-solid mechanism (VLS) and their microstructural and phase change memory (PCM) properties characterized. Low reset power ($\sim 400 \mu\text{W}$) and fast set and reset (25 ns) were demonstrated.

#P018 - Broadband Light Trapping in Nanotextured Optoelectronic Devices

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Broadband Light Trapping in Nanotextured Optoelectronic Devices

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We propose the use of nanotextured interfaces in view of light manipulation in optoelectronic and photovoltaic devices. The final aim is to achieve light coupling across interfaces of dissimilar material employed in photonics devices exploiting broadband light scattering properties of one-dimensional pseudo-periodic self-organized gratings. We experimentally demonstrate large area (cm^2) and high

aspect-ratio nanopatterning of substrates by recurring to de-focused ion beam sputtering (IBS) through a self-organised sacrificial Au nanowire stencil mask. These nanoscale features, can be obtained on different substrates ranging from glass, transparent conductive oxides, metals and crystalline semiconductors like Si and GaAs [1]. Textured substrates have been characterized from the morphological and optical point of view by means of an AFM microscope and an integrating sphere, respectively. Morphological parameters have been employed to simulate and analyze the optical response of textured glass by recurring to 3D finite difference time domain (FDTD) method. Pseudo periodic one-dimensional nanostructures endowed with high aspect ratio proved numerically and experimentally to be effective in view of broadband diffuse scattering of radiation. Haze values (around 30%) higher than commonly employed light trapping reference materials are reported. Thin film solar cell based on the nanostructured pattern has been numerically studied for broadband absorption enhancement using the 3D FDTD and compared with the experimental outcome of physical devices. Tangible absorption enhancement is reported in nanostructured devices relative to the conventional flat thin film solar cell. The optimized SC can offer a short circuit current of 13.8 mA/cm² with an enhancement of 21% over the SC without textured surface [2]. We will also discuss recent developments involving use of organic solar cells and the application of bio-mimetic antireflection texturing obtained by laser interference lithography.

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#P019 - Hydrogels based on hyaluronic acid/cyclodextrin assemblies for regenerative medicine

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HYDROGELS BASED ON HYALURONIC ACID/CYCLODEXTRIN ASSEMBLIES FOR REGENERATIVE MEDICINE

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In the past few years, extensive research has been done to develop proper drug delivery platforms that can deliver therapeutic agents to specific sites of the body or targeted cells, minimizing side effects. Similar to the microenvironment of soft tissues, hydrogels are a novel type of delivery platform with a 3D interconnected structure formed by physically or chemically cross-linked polymer networks. Drugs can be incorporated in the tridimensional scaffold and successfully vehiculated/administered into specific sites of the organism¹.

Hyaluronic acid (HA) is a high molecular weight negatively charged polysaccharide composed of repeating disaccharide units, which is abundant in the synovial fluid and extracellular matrix, but has also been found intracellularly. HA is involved in several biological processes such as the maintenance of the viscoelasticity of connective fluids, tissue hydration, morphogenesis and cell repair². For these reasons it represents a valid biomaterial for tissue engineering as component of hydrogel platforms, thanks further to its good biocompatibility, biodegradability and non-immunogenicity.

Currently, we are exploring the best experimental conditions to obtain a hydrogel scaffold formed by the interactions between an amphiphilic network (HA-TDA) and a cationic cyclodextrin polymer (Poly-CD). Once formed, the construct can potentially incorporate various therapeutic cargos (i.e. drugs, growth factors, exosomes, cell adhesion promoters) and diagnostic probes (i.e. fluorophores and magnetic nanoparticles), to be used as cell-laden material for bioprinting in regenerative medicine applications³.

HA-TDA was synthesized by coupling of hydrophobic tetradecylamine (TDA) to hyaluronic acid (HA) in the presence of 2-chloro-4,6-dimethoxy-2,3,5-triazine (CDMT) and *N*-methylmorpholine (NMM). Complementary spectroscopic techniques such as UV-Vis, steady-state and time-resolved fluorescence, DLS and z-potential measurement have been used to investigate the interactions and to monitor the assembly between HA-TDA and Poly-CD at different mass ratios and the entrapment capability of HA@CD assembly.

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#P020 - Doping organic semiconductors: giant vibrational modes in polymers and interface excitations in molecular crystals.*Enrico Da Como - University of Bath**Other Authors: Marie Anderson (Univ. of Bath) Gabriele D'avino (Inst. Neel, Grenoble) Achidi Frick (VU Amsterdam) Elizabeth von Hauff (VU Amsterdam) Claudio Fontanesi (Univ. Modena e Reggio Emilia)*

Modulation doping, i.e. transfer of charge from dopants spatially separated from the semiconductor, is an effective way to minimize the impact of scattering by ionic impurities on charge carrier mobility. This concept, first introduced in inorganic heterostructures, has been lately applied to polymeric and single crystal organic semiconductors by depositing dopants on the polymer surface [1] or laminating single crystals heterojunctions [2].

We show how surface doping of the conjugated polymer PCPDTBT by the dopant F6-TCNNQ provides high optical quality thin films suitable for spectroscopy in a broad frequency range spanning from the mid IR to the UV. This allows us to gauge the intensity of molecular vibrations linked to on chain polarons. Their giant intensity is demonstrated to arise from the displacement of charge density by specific topological vibrational modes [3].

The surface of high quality single crystals of the organic semiconductors tetracene and perylene has been doped with thin films of F4-TCNQ. By optical reflectance spectroscopy we show how the surface excitations are modified as a consequence of interfacial charge transfer in 2D.

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#P021 - Flame Spray Pyrolysis for oxides nanoparticles synthesis*Silvana De Iuliis - CNR-ICMATE, Institute of Condensed Matter Chemistry and Technologies for Energy**Other Authors: F. Migliorini, CNR - ICMATE; K. Biancardi, Università Milano Bicocca; R. Donè, CNR - ICMATE; A. Strini, CNR - ITC; L. Schiavi, CNR - ITC*

Flame spray pyrolysis (FSP) process is considered as a powerful method to produce nanoparticles oxides with different properties. In particular, the ability to change the experimental conditions in the flame can be very helpful for the synthesis of single- and multi-component nanoparticles with specific and tailored characteristics. Properties such as crystallite size, crystalline phase, degree of aggregation and agglomeration, surface area and porosity can be very challenging in different applications including catalysis, gas sensors as well as energy storage.

The flame spray pyrolysis apparatus developed in CNR Milano laboratory consists of an oxygen-assisted spray used to inject the liquid precursor, which is normally fed by a syringe pump. A pilot flame, positioned coaxially to the flame spray, allows starting combustion reactions.

The apparatus has been designed and developed in order to produce nanoparticles in powder as well as in film. The availability of powder supported deposits is very useful for catalytic applications (e.g. air and water treatment), to overcome several problems of process design and implementation. During the synthesis, the powder is collected on a filter, whilst the nanoparticles deposition is obtained by orthogonal impingement on a cooled (100°C) substrate holder (alumina or stainless steel) positioned at 30 cm height above the burner. A pneumatically operated mechanical shutter placed above the target substrate allows the control of the exposure time of the aerosol-generated powder deposition. Temperature measurements along the synthesis process is properly changed and monitored in order to obtain nanoparticles of particular chemical and physical characteristics. After synthesis, an annealing process of the film is performed in order to improve film-substrate adhesion.

Synthesis of TiO₂ are performed with this method and then characterised by means of XRD, STEM and FT-IR analysis. In particular, size and phase of the nanoparticles and the related deposits have been investigated changing the experimental conditions of the reactor. Moreover, as for the titania films, the photocatalytic activity has been evaluated by measuring the degradation of toluene in air at typical environment concentration using a stirred flow photoreactor operated at constant concentration under UV-A irradiation.

The results prove the potentials of the method as a scalable technology for synthesis of advanced materials in powder as well as powder supported deposit.

#P022 - Mechanim of light induced reactions of DASA photoswitchs*Mariangela Di Donato - LENS**Other Authors: Michael M. Lerch (Centre for Systems Chemistry, Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands), Andrea Lapini (INO-Istituto Nazionale di Ottica, Largo Fermi 6, 50125 Firenze, Italy), Adèle D. Laurent (CEISAM, UMR CNRS 6230, BP 92208, 2 Rue de la Houssinière, 44322 Nantes, Cedex 3, France), Alessandro Iagatti (LENS via N. Carrara 1, 50019 Sesto*

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Donor-acceptor Stenhouse adducts (DASAs) are negative photochromes that hold great promise for a variety of applications. An important step to optimize their switching properties is a detailed understanding of the photoswitching mechanism. We have fully characterized the actinic step of DASA-photoswitching using ultrafast pump-probe spectroscopies, both in the visible and infrared spectral range. The interpretation of experimental outcomes was supported by TD-DFT computations. Comparison of the time-resolved IR spectra with DFT computations allowed to unambiguously identify the structure of the important photogenerated intermediate, produced on a fast timescale of a few picoseconds, indicating that light absorption induces a sequential reaction path in which a *Z-E* photoisomerization of C₂-C₃ is followed by a thermal cyclization step. First and second generation DASAs share a common photoisomerization mechanism in chlorinated solvents with notable differences in kinetics and life-times of the excited states.¹ The photogenerated intermediate of the second generation DASA was photo-accumulated at low temperature and probed with time-resolved spectroscopy, demonstrating the photo-reversibility of the isomerization process. Furthermore, we showed that the actinic step of DASA photoswitching is the same, irrespective from the solvent,² and that the hydroxyl group present on DASA's molecular structure plays an important mechanistic role.³ Taken together, these results provide a detailed picture of the DASA isomerization pathway on a molecular level.

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#P023 - Effect of H⁺ irradiation on magneto-optical properties of Co-doped ZnO thin films

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We present an investigation on the strong magneto-optical response exhibited by ferromagnetic Co-doped ZnO films upon hydrogen ions irradiation. Magneto-optical thin film materials with high figure of merit (i.e. high ratio of Faraday rotation per unit length to the optical loss per unit length) can pave the way for development of new integrated on-chip non-reciprocal photonic devices. Most efforts are currently directed to the growth of films of ferromagnetic garnet oxides which are however very difficult to integrate in optoelectronic technologies. In such a context, we show that ZnO-based diluted magnetic semiconductors obtained by incorporating transition metal elements (e.g. Fe, Co) are suitable for the purpose.

Ferromagnetic behaviour of Co-doped ZnO films can be improved when treated by a suitable atomic hydrogen treatment [1]. We investigated the role of hydrogen in the improvement of the magneto-optical properties by comparing the magnetic circular dichroism spectra of H-irradiated ZnCoO films. Optical and microstructural analyses indicate that Co fully substitutes for Zn ions without phase segregation. In addition to a large increase in the saturation magnetization we observe larger values of the magnetic circular dichroism upon hydrogen incorporation, especially for the samples processed with high H-doses which also show a large value of the Faraday rotation at magnetic saturation.

These results give a direct indication of the intrinsic nature of the ferromagnetism in this class of materials as arising from the spin polarized carriers magnetically coupled to Co ions. The values of the Faraday rotation and hence the figure of merit of the hydrogenated films in the *vis* range can be tuned by a suitable choice of the H-dose and are promising in the perspective of non-reciprocal magneto-optical devices integrated on semiconductors.

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#P024 - Correlation between Creep and Relaxation Behaviour in a Cr Martensitic Steel

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There is a growing number of papers in literature concerning the possibility, for high temperature component design purpose, to generate creep rate data using stress relaxation tests and viceversa. According to these papers, relatively short stress relaxation tests could allow to estimate the creep strain rates spanning in several decades. Similarly, quite simple and inexpensive creep tests could predict stress relaxation performances.

In order to check if stress relaxation tests can be a quick experimental way to obtain long term creep data, the primary creep and stress relaxation behaviour of a martensitic steel, has been investigated at 350°C with tests lasting up to 15.000h. Different kind of stress relaxation tests have been performed, in particular:

- multiple stress relaxation tests where the specimen, after some stress relaxation, is reloaded at the initial load and stress relaxed again,
- stress relaxation tests performed on specimens crept up to the steady state.

The experimental results show that anelastic-reversible-kinematic hardening processes control the initial stages of creep and relaxation, while creep-irreversible-isotropic hardening mechanisms control the creep and relaxation behaviour at longer times. The results indicate that the experimental curves obtained in multiple stress relaxation tests can give important information on the steady state creep behaviour of the alloy.

Finally, the experimental results have been modelled using coupled differential equations of the Kachanov form, that are consistent with physical deformation mechanisms of the studied alloy.

The parameters of the proposed constitutive equation are functions of microscopic parameters like the density of mobile dislocations and their curvature between pinning points, but they are also related to easily measurable characteristics of the experimental creep curves, so that they can be determined using macroscopic creep data only.

The use of differential formalism of the equations allows to describe the creep behaviour also at variable stress and temperature, and to cope also with more complicated load/temperature histories as, for example, variable loading creep, constant strain rate and stress relaxation tests without appealing to arbitrary strain or time hardening rules.

In order to further validate the proposed equations, creep tests with one step change of load and/or temperature have been performed.

The proposed differential equations have been successful both in interpolating the constant load/temperature tests and in predicting the stress relaxation behaviour and the effect of step changes in load on the creep behaviour of the alloy.

#P025 - Coherency and anharmonicity in flexural phonons of graphene: a simulation study

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Graphene sustains transverse out of plane acoustic phonons (the ZA branch), also called “flexural”, characterized by a quadratic dispersion near the Brillouin zone center for symmetry reasons. In this work we analyze how thermal effects and anharmonicity affect the behaviour of ZA phonons by means of classical mechanical molecular simulations with Tersoff empirical force field with parameters optimized to reproduce the ZA branch. The vibrational properties (frequency and modes eigenvectors) are evaluated either with Fourier transforms or Principal Component Analysis of simulation trajectories implemented in in-house codes. The specific aim is to separate the intrinsic anharmonic effects due to the increase of the phonon amplitude from those due to the thermal coupling. This study is motivated by the possibility to generate traveling ripples or cavities to move actively and pump gases (f. i. hydrogen), if coherent ZA phonons of given wavelength and high amplitude in counter-phase in alternate multilayers are maintained. For this reason, the degradation of the coherency must be considered in the design of a practical device.

#P026 - How Nature Disguises Chirality in Chiral Functional Nanostructures

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Examination of protein 3-dimensional structures suggests that complex tertiary folds and quaternary associations can be deconstructed into a limited number of secondary structural elements, such as strands, helices, and turns, which are assembled using loosely structured loops. Those structures direct the sophisticated functions of proteins in living systems. Inspired by biological structures, chemists have worked to synthesize polymers with controlled helicity, not only to mimic the biological helices but also to realize their functions. The increasing amount of knowledge acquired from recent studies on elastomeric proteins has inspired the design and synthesis of biopolymers with interesting mechanical and biological properties. However, a lack of detailed understanding of the molecular folding mechanisms of these proteins limits the structure-based manipulation of related mechanical properties. We are interested in the synthesis, structure and function of hetero- and homo-chiral biopolymers able to assume specific ordered structures Elastomeric

proteins are present in a wide range of biological systems, where they have evolved to meet specific functional needs. The ability of any protein to exhibit elasticity lies in its molecular and structural organization: individual components must be conformationally free so that they can respond quickly to the applied stress and they must form an inter-connected network of chains through covalent or no covalent crosslink, to effectively distribute the applied stress throughout the structure. The elastic properties of such proteins depend on the nature of elastomeric domains, the size of the domain and the degree of crosslinking. Here we present preliminary results on conformational behaviour of polymerizable subunits in which type II β -turn act as spacer between hydrophobic segments having high propensity to form β -helix.

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#P027 - Ab-initio investigation of a novel photocathode: bulk and surface properties of CuFeO₂.

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The urgent need to transition from fossil fuels to renewable energy sources is driving several avenues of intense research. Photoelectrochemical (PEC) devices offer the possibility to convert solar radiation into chemical fuels, mimicking the natural process of photosynthesis.

Recent experiments have highlighted the delafossite CuFeO₂ (CFO) as a promising candidate in the role of the photocathode [1,2], yet in spite of these encouraging results, improvement in the catalytic activity and charge separation is required. An adequate theoretical characterization is currently not available to provide insight that can direct further experimental investigations.

In this work, we present the first fully self-consistent Hubbard U investigation of CFO using the linear response approach introduced and refined by Cococcioni, De Gironcoli, Kulic, Scherlis and Marzari [3,4]. On this basis we characterize both the geometric and the electronic properties of the bulk CFO for a range of magnetic configurations, with results suggesting that, like other Fe-oxides, the antiferromagnetic arrangement of spins inside each layer is favored.

The band edge alignment at the CFO/water interface is fundamental for PEC applications. For this reason it is necessary to go beyond the bare bulk properties, thus we also report on the low-Miller index surfaces exposed to the vacuum. The most stable surface at equilibrium with atomic reservoirs is the one that minimizes the free-energy at constant temperature and pressure. To mimic the surface, for each orientation, slabs with different number of layers and different termination have been considered, accounting for the possibility of defects in the structure. An ab-initio thermodynamics investigation of the surfaces, evaluating the surface energy for different values of the chemical potential of the atomic species, reveals the (11-20) surface is energetically favored with the possibility to create Fe vacancies at the surface.

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#P028 - Carbon Monoxide uptake on pristine and Nitrogen-doped graphene overlayers on Ni(111)

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Carbon monoxide (CO) is one of the most devious and potentially lethal gases, which requires the development of new and extremely sensitive detectors for daily life safety. Despite graphene attracted a significant interest for gas sensing applications, DFT calculations report only a weak interaction between CO and a perfect graphene layer [1], making graphene not suitable for CO detection.

Nevertheless defected and/or doped graphene overlayers show an increased interaction to CO [2], and theoretical calculations report Nitrogen (N) doped graphene as a good candidate for CO sensing [3].

Here we investigate how pristine and N-doped graphene overlayers grown on a Ni(111) surface are morphologically and chemically modified when exposed at room temperature (RT) to different CO pressures, from 10^{-3} Torr up to near ambient pressure (10 Torr). The measurements were performed in ultra high vacuum (UHV) conditions, using different experimental techniques like scanning tunneling microscopy (STM), photoemission spectroscopy and low energy electron diffraction (LEED).

Our data show that N-doping facilitates CO intercalation, lowering the minimum required pressure from 500 mTorr (for pristine graphene) to 1 mTorr. Intercalated CO forms a stable long-range ordered adsorption structure on the underlying Ni(111) substrate, decoupling the graphene layer. On the other hand, intercalated CO in between graphene and Ni₂C is demonstrated to be weakly interacting with the substrate and to be hardly confined by graphene.

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#P029 - PPTF vs PPF: two high gas barrier bio-based polyesters for packaging applications

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Packaging plays a key role in the protection and preservation of foods. Many efforts are currently lavished on the study of gas barrier bioplastics as substitutes of traditional fossil-based polymers. Two 100% biobased aromatic polyesters, poly(propylene 2,5-thiophenedicarboxylate) PPTF and poly(propylene 2,5-furandicarboxylate) PPF, were successfully synthesized by two stage melt polycondensation, in a solvent-free synthetic approach, easily to scale up at industrial level. They differ in the diacid sub-unit, PPF containing the furan ring, PPTF the thiophen one. Both have been characterized from the molecular, thermo-mechanical, structural point of view and the gas permeability behavior has been measured with respect to 100% oxygen, carbon dioxide and nitrogen at different temperatures and relative humidity. PPTF and PPF are characterized by outstanding gas barrier performances with respect to poly(ethylene 2,5-furanoate) PEF and poly(ethylene terephthalate) PET. The different crystallizing ability and the different gas barrier properties suggest packaging applications in different areas: PPTF being preferable with a temperate climate, PPF in tropical regions.

#P030 - Development and characterization of xyloglucan-poly(vinyl alcohol) hydrogel membrane for wireless smart wound dressings

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Research which addresses advanced wound management can contribute to the needs of modern healthcare, especially in situations that require continuous monitoring, analysis, responsive therapeutic treatments and data recording. The development of "smart" bandages and dressings that can remotely monitor relevant parameters for the wound healing process without a hospital intervention can be very useful tools for patients and physicians and for advancing the understanding of the healing process. In the present work, biocompatible xyloglucan/poly(vinyl alcohol) hydrogels are being developed as smart wound dressings that, in addition to the traditional favorable properties of hydrogels as skin care material, can sense relevant biological parameters and provide support for remote monitoring of wound healing itself. The swelling behavior of the films by simulated biological fluids and the induced changes of their dielectric properties in a wide range of frequencies (10^0 - 10^6 Hz and 10^8 - 10^{11} Hz) are investigated. The highest frequency band is particularly relevant for the optimization of UHF RFID smart dressings. The swelling-induced microstructure and rheological properties modifications are also evaluated by SEM microscopy and dynamic mechanical measurements, respectively. The films absorb simulated

body fluids up to approximately four times their initial dry weight, without losing their integrity but undergoing significant microstructural changes. We observed relevant linear increases of electric conductivity and permittivity with the swelling degree, with an abrupt change of slope that is related to the network rearrangements occurring upon swelling.

A parallel biological study on the same hydrogels films is demonstrating that they are non-cytotoxic, fully hemocompatible, non-adhesive to the wound and able to provide protection from bacterial infiltration. These results altogether encourage in proceeding with further development and evaluation of these hydrogel membranes as smart wound dressings.

#P031 - Low-resistance ohmic contacts on n-type Sn-doped ϵ -Ga₂O₃ thin films

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ABSTRACT: The different crystallographic phases (α , β , γ , δ , and ϵ) of gallium oxide (Ga₂O₃) have been widely studied in the last years. Between these, the monoclinic β -Ga₂O₃ is the most investigated due to demonstrated applications in the deep-UV and power electronic fields¹. However, the orthorhombic ϵ -phase is also attracting attention thanks to its wide bandgap (4.6÷4.8 eV), higher crystallographic symmetry and lower deposition temperature than the β -phase. In this paper we will present the n-type doping obtained by diffusing Sn in nominally undoped ϵ -Ga₂O₃ layers. We will also report the analysis of different types of electrical contacts on this n-type material. This study allowed us to find an ohmic behavior. The starting undoped layers were grown at (600÷610) °C by Metal-Organic Vapor Phase Epitaxy (MOVPE) on c-oriented sapphire substrates. For doping, a two steps procedure was developed: first, a thin layer of Sn, 50 nm thick, was deposited by R.F. sputtering on the undoped epilayers and, second, an annealing of 4 hours at 600°C was performed. After the diffusion-made doping, the resistivity of ϵ -Ga₂O₃ reached values in the range (5÷10) Ω cm. For the ohmic contact study, the Sn-diffused layers were chemically etched with HF+HNO₃ (50:50) in order to remove the residual tin oxide on the surface before depositing three different types of contacts (Ti-Au, AZO-Ti-Au² and ITO-Pt³) by sputtering. I-V characteristics were performed on each sample after annealing the contacts at a temperature ranging from 300°C to 500°C. A good ohmic behaviour was found after one-minute annealing of ITO-Pt contact at 400°C.

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#P032 - A NOVEL 3D ARSENIC MOLYBDENUM OXIDE WITH LAYERED CHARGE DISTRIBUTION

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There is a great interest on synthesis and characterization of engineered molybdenum oxides because of their importance in physics of devices as possible high work function hole-injection materials for organic/inorganic interfaces.

We obtained single crystals of a novel 3D framework nanoporous Molybdenum oxide, As₂Mo₁₀O₃₁, based on mixed valent (Mo⁺⁵, Mo⁺⁶)O₆ octahedral network in which (As⁺³) cations are located in low dimensional channels. The crystals of As₂Mo₁₀O₃₁ were grown by vapor phase transport process. This stoichiometric oxide has a crystal structure classified as a (2)-Intergrowth Tungsten Bronze [(2)-ITB] (space group: *Pma*2 and unit cell parameters: *a* = 20.1906(9), *b* = 8.0044(3), *c* = 7.1931(3) Å).

High Resolution TEM (HRTEM) images and electron diffraction patterns are in perfect agreement with the crystal structure data determined by single crystal X-ray diffraction technique. The crystals show a high grade of crystallinity: no intergrowth boundaries or impurity were detected in HRTEM observations. The semi-quantitative Energy Dispersive X-ray Spectroscopy (EDS) analysis exhibit an atomic ratio Mo/As close to 5.

The crystal morphology has been analyzed by AFM imaging performed in air, showing nearly atomically flat faces in the micrometer scale (RMS area roughness *S_q* ~ 0.7 nm) with apparent sharp steps around 1 nm high. Elongated ridge-like features with non-random reciprocal orientations were also sparsely present on the crystal surface.

Low temperature EPR spectroscopy showed a strong paramagnetic signal proving the presence of (Mo^{+5}) active centers. The vibrational and optical spectroscopies (polarized micro-Raman, Infra-Red and NiR/Vis/UV absorption) confirmed a strong polarization in Raman signal and high optical absorption.

The band structure of this [(2)-ITB] arsenic molybdenum oxide was calculated by Density Functional Theory (DFT) methods, together with the total and projected density of states. The internal electron density turned out to be layered and segregated in the *ac*-plane, resulting in a quasi-2D charge distribution. A good agreement with experimental optical transition was obtained.

Keywords: 3D molybdenum oxide, single crystal X-ray diffraction, HRTEM, EPR, Polarized micro-Raman, DFT, Band structure.

#P033 - A NOVEL 3D ARSENIC MOLYBDENUM OXIDE WITH LAYERED CHARGE DISTRIBUTION

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There is a great interest on synthesis and characterization of engineered molybdenum oxides because of their importance in physics of devices as possible high work function hole-injection materials for organic/inorganic interfaces.

We obtained single crystals of a novel 3D framework nanoporous Molybdenum oxide, $\text{As}_2\text{Mo}_{10}\text{O}_{31}$, based on mixed valent (Mo^{+5} , Mo^{+6}) O_6 octahedral network in which (As^{+3}) cations are located in low dimensional channels.

The crystals of $\text{As}_2\text{Mo}_{10}\text{O}_{31}$ were grown by vapor phase transport process. This stoichiometric oxide has a crystal structure classified as a (2)-Intergrowth Tungsten Bronze [(2)-ITB] (space group: *Pma2* and unit cell parameters: $a = 20.1906(9)$, $b = 8.0044(3)$, $c = 7.1931(3)$ Å).

High Resolution TEM (HRTEM) images and electron diffraction patterns are in perfect agreement with the crystal structure data determined by single crystal X-ray diffraction technique. The crystals show a high grade of crystallinity: no intergrowth boundaries or impurity were detected in HRTEM observations. The semi-quantitative Energy Dispersive X-ray Spectroscopy (EDS) analysis exhibit an atomic ratio Mo/As close to 5.

The crystal morphology has been analyzed by AFM imaging performed in air, showing nearly atomically flat faces in the micrometer scale (RMS area roughness $S_q \sim 0.7$ nm) with apparent sharp steps around 1 nm high. Elongated ridge-like features with non-random reciprocal orientations were also sparsely present on the crystal surface.

Low temperature EPR spectroscopy showed a strong paramagnetic signal proving the presence of (Mo^{+5}) active centers. The vibrational and optical spectroscopies (polarized micro-Raman, Infra-Red and NiR/Vis/UV absorption) confirmed a strong polarization in Raman signal and high optical absorption.

The band structure of this [(2)-ITB] arsenic molybdenum oxide was calculated by Density Functional Theory (DFT) methods, together with the total and projected density of states. The internal electron density turned out to be layered and segregated in the *ac* plane, resulting in a quasi-2D charge distribution. A good agreement with experimental optical transition was obtained.

Keywords: 3D molybdenum oxide, single crystal X-ray diffraction, HRTEM, EPR, Polarized micro-Raman, DFT, Band structure.

#P034 - Glassy behaviour of light: numerical simulations of the electromagnetic field interactions in a disordered medium

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It has been recently proposed that the fluctuations in the emission spectra of random lasers can be understood in terms of a thermodynamic phase transition to a glassy phase: this is a regime where the amplitudes and phases of light normal modes are frozen in the same disordered configuration for the whole duration of the pulse. So far the only analytical predictions on the thermodynamics of this phase have been obtained in the so-called narrow band approximation, that is by assuming a light-modes interaction network that is fully connected and in whose constitution the mode frequencies play no role at all.

We present the first numerical results, obtained from highly optimized GPU-codes, showing that the thermodynamic glass transition with the features predicted by the mean field models is, indeed, present even when the light modes are put on the less dense and correlated network, termed mode-locking graph, best reproducing the true interaction network. We are therefore able to interpolate between the state of the art of experimental results on glassy random lasers and the recent analytic results on the related statistical mechanical models with frustrated mode couplings.

#P035 - Optically transparent microwave antennas based on engineered CVD graphene

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We report on radiation elements, operating over a wide microwave operating bandwidth (> 3.5 GHz) simultaneously covering the WiFi, Bluetooth and 5G bands, that exploit highly conductive Chemical Vapour Deposition graphene [1-3]. In particular, the design of a wide planar CVD graphene-based antennas will be detailed. At microwave frequencies (e.g. L, S or X microwave bands) monolayer graphene thickness, equal to 0.34 nm, corresponds to about $\lambda/106$. Thus, monolayer or few-layer graphene act as a real "sheet current" with a finite conductivity. A 3D numerical model in Comsol Multi-Physics is developed where graphene is modelled as a sheet current ($J = \sigma E$) with a finite conductivity (where σ is equal to $1/R_s$). We demonstrate that CVD graphene can successfully exploited for the realization of flexible and optically transparent antennas (transmittance of about 85%). The -10dB bandwidth is wide enough to cover the several microwave frequency ranges. Another important feature offered by graphene antennas is related to the tunability of graphene transport properties, i.e. the "ambipolar effect". This last feature could open the way to realize tunable antenna arrays for beam-steering (or beam-forming) applications. The combination of all the CVD graphene properties (transparency, flexibility and tunability) could be strategic for the integration of graphene antennas in photovoltaics, security, military and healthcare applications systems.

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#P036 - Stimuli responsive PGA Nanoparticles as safe agents for non viral gene delivery

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Nanoparticle (NP)-based therapeutic systems developed in recent years have shown efficient delivery of drugs and/or nucleic acids with low toxicity and sustained cargo release.

Recently, more attention has been paid to stimuli sensitive delivery systems that are promising strategies for active agent release. Many techniques have been developed to produce systems that could be used for effective encapsulation of active agents, as drugs or genes. External and internal stimuli, such as temperature, [1] pH, [2] light, [3] and protease, [4] could be utilized to control the active agent release in delivery systems. Among all these strategies, release systems based on pH variation have obtained more attention, because the pH difference between different intracellular compartments could be used for targeting systems design.

For gene delivery application, NPs can accommodate large DNA plasmids, RNA or proteins and may be produced at low cost on a large scale. NP-based systems overcome safety problems and limitations of viral vectors. FDA-approved polymers are particularly attractive for *in vivo* drug/gene delivery applications. Recently, we have developed a polymeric system for drug and gene based on pH-responsive, core/shell NPs using the FDA approved PCL polymer. [5-8]

Another, attractive polymer for gene delivery applications is polyglycolic acid (PGA), which has been approved by the FDA. PGA degradation is quicker *in vivo* and *in vitro*, and the degradation product, glycolic acid, is non-toxic and it can enter in the tricarboxylic acid cycle.

For gene delivery, we have developed pH-responsive core-shell polymeric NPs showing that they mediate efficient cDNA delivery. Our PGA NPs with size about 300 nm, obtained by the emulsion-diffusion-evaporation method, are composed of a core with DNA molecules and a PGA shell.

Using PGA NPs loaded with GFP cDNA in different cell lines, we observed relative numbers and mean fluorescence intensity of transfected GFP-positive cells comparable to those achieved with standard reagents used to promote transfection.

PGA NPs, thanks their properties, as biocompatibility, biodegradability and a good transfection efficacy, can be used as efficient tool of transfection overcome viral vector problems.

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#P037 - Novel nanostructured gold counter electrodes for DSSCs prepared by pulsed laser ablation

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Dye-sensitized solar cells (DSSCs) are receiving increasing interest as a viable technology for the conversion of sunlight into electricity thanks to their low cost and lightweight. At present, in order to improve the efficiency of the DSSCs, the attention has been mainly focused not only on the chemical modification of the dye, but also on the production of different kinds of counter electrodes.

In this study, the applicability of pulsed laser ablation (PLA) for the production of nanostructured gold counter electrodes for DSSCs has been investigated. With pulsed laser ablation a wide range of morphologies such as arrays of randomly distributed nanoparticles and semi-percolated structures can be obtained by changing the deposition parameters, notably argon pressure and the number of laser pulses on the target.

Nanostructured gold counter electrodes were prepared focusing a KrF excimer laser (248 nm) on a rotating gold target with 30000 laser pulses under a 100 Pa argon pressure: a network of coalesced islands with smoothed edges was found on the substrate.

SEM images, absorption spectra and electrochemical studies were performed to characterize the nanostructured gold counter electrodes. The photovoltaic parameters of the DSSCs assembled with these cathodes show that they are a viable alternative to platinum.

#P038 - Illuminating Correlative Battery Research using Light, X-ray and Electron Microscopy

Lars-Oliver Kautschor - Carl Zeiss Microscopy GmbH

X-ray tomography has emerged as a new powerful imaging technique that obtains 3D structural information from opaque samples under a variety of conditions and environments. It has rapidly become an accepted laboratory technique offering quantitative information in materials science. With batteries application examples, we present ways in which non-destructive 3D volumetric information, obtained via laboratory nanoscale and sub-micron X-ray microscopy (XRM) are increasingly used to probe scientific questions as a complement to Electron- and Light-based microscopy methods. These correlative methods, relating to XRM, provide an opportunity to study materials evolution at multiple length scales in 3D and utilize this information to inform or guide postmortem analysis to be most efficient.

#P039 - Speeding up research: An easy way to quickly find and use materials property data

Michael Klinge - Springer Nature

SpringerMaterials (materials.springer.com) is the largest database in the fields of physics, chemistry, and materials science. It contains critically evaluated property information about 290,000 materials and substances and is based on the prestigious Landolt-Börnstein book series. With the help of computational methods, developed by materials scientists at Duke University and the University of North Florida, traditional book content in the fields of thermophysical properties as well as semiconductors/materials for energy applications has been digitized. This digitization and the subsequent development of interactive functionalities help scientists in university and industry in the above mentioned fields to better find, use, and interact with reliable property data. Initial results will be presented.

#P040 - Osteogenic and antibacterial properties of hydroxyapatite with multiple ion doping

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Introduction

A serious concern related to the implantation of biomedical devices such as prostheses, catheters, stents, is the occurrence of post-surgical infections [1]. Particularly, infections associated to bone implants frequently degenerate into osteomyelitis, a severe clinical problem, very difficult to be completely eradicated [2, 3]. In this respect the development of new materials integrating the ability to promote and sustain bone regeneration with prolonged and effective protection against bacteria is a topic of great relevance in bone surgery. Hydroxyapatite (HA) is the elective material for bone substitutes, and specific ion doping, particularly magnesium and carbonate ions, provide apatite with enhanced ability of inducing new bone formation. In this respect the present work describes the synthesis of novel multi-doped apatite phases with enhanced osteogenic and antibacterial ability. In particular, extensive physico-chemical and biological characterization assessed the effect of gallium or zinc doping in reducing the activity of several bacterial strains, and the enhancement of antibacterial and osteogenic effect, as induced by simultaneous co-doping with Mg and CO₃ ions, and the continuous release of these ions in the culture media.

Materials and Methods

Apatite phases exhibiting single and multiple ion doping (i.e. with Ga or Zn and additional Mg and CO₃ ions, in different amounts) were synthesized by neutralization method. The new materials were characterized by ICP and XRD analysis to evaluate the effect of the different doping on the apatite crystal features. Then, in vitro analysis of human mesenchymal stem cells (MSCs) behaviour, and of the activity of four different infective agents (*C. Albicans*, *E. Coli*, *P. Aeruginosa*, and *S. Aureus*) was carried out and correlated with the extent of ion release in the same medium, to elucidate the active mechanisms in bacterial inactivation.

Results and Discussion

Rietveld analysis of XRD patterns demonstrated the effect of single and multiple doping on the cell parameters and crystal domains of the apatite lattice in the new materials. The single doping with Ga or Zn ions provided enhanced antibacterial activity, in respect to undoped HA whereas multiple doping including also Mg and CO₃ gave enhanced effect, associated with higher cell viability and ALP expression by MSCs.

Conclusions

The new multi-doped apatites are promising materials to develop bone implants and coatings simultaneously showing improved effect on new bone formation and prevention of bacterial infections.

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#P041 - Phosphonate-Substituted Conjugated Polymers for Interfacial Engineering in Polymer Solar Cells

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Interfacial engineering has been identified as a fundamental strategy for maximizing the performances of organic electronic devices, such as light emitting diodes and organic solar cells. To this aim, water/alcohol soluble materials comprising a π -conjugated backbone with pendant polar or ionic groups demonstrated to be quite effective as cathode interfacial layer (CIL), since they combine several advantages including: orthogonal solubility to solvent used to process the active layer, robust film formation, chemical flexibility in tailoring both the conjugated backbone as well as the polar/ionic functionalities. Among the polar side groups so far proposed to design CIL materials, phosphonate moieties have shown excellent interactions with aluminum electrode and inorganic semiconductors as indium tin oxide and zinc oxide [1-3]. Good interaction between ZnO nanoparticles (NPs) and phosphonate groups can be exploited to develop hybrid ZnO:polymer composite [3]. In this work, we have designed and synthesized a series of copolymers featuring phosphonate pendant groups. Their functional behaviour as cathode modifiers in polymer solar cells is herein investigated, for both pristine films and hybrid ZnO:polymer composites.

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#P042 - Insoluble rust waste as inorganic precursor for Fe-containing perovskite-type materials prepared by solution combustion synthesis

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Recycling of waste has gained increasing importance in our society. Moreover, a sustainable production of catalytic materials is highly desirable in all the industrial processes. In comparison with organic waste, inorganic waste such as rust waste is much more complicated to recycle directly and usually require complex extraction procedures [1]. For the first time, insoluble rust waste from an electricity transmission tower manufacturing industry was directly used as Iron source for the preparation of LaFeO_3 perovskite-type compounds by solution combustion synthesis [2] in place of the commercial Iron nitrate. Commercial Lanthanum nitrate was used as a source of Lanthanum. The waste derived-Iron precursor and the obtained LaFeO_3 powders were characterized by several techniques, such as microwave plasma - atomic emission spectroscopy, powder X-ray diffraction coupled with Rietveld refinement, N_2 adsorption, temperature programmed reduction, X-ray photoelectron spectroscopy and scanning electron microscopy. For a stoichiometric Lanthanum amount, the effect of the waste derived -Iron precursor content on the powders properties was studied in details and the performance of these ecofriendly perovskite-type materials was evaluated in the catalytic oxidation of propene, that is harmful for the environment due to its high photochemical ozone creation potential (POCP). A comparative study of the catalytic activity, in terms of propene conversion to CO_2 , was conducted with a LaFeO_3 powder obtained from a commercial Iron nitrate precursor. Results showed that rust waste was composed mainly by metallic Iron and mixed Iron oxides. For low and for high Iron precursor contents, respectively, a $\text{LaFeO}_3\text{-La}_2\text{O}_3$ or a $\text{LaFeO}_3\text{-Fe}_2\text{O}_3$ nanocomposite was produced. A pure LaFeO_3 was obtained, already in the as-burned powders, for a stoichiometric amount of the precursors. This ecofriendly strategy allows producing Iron perovskites with identical catalytic activity and higher benefit for the environment, with respect to those obtained from the commercial iron precursor. $\text{LaFeO}_3\text{-Fe}_2\text{O}_3$ nanocomposites have slightly lower catalytic activity with respect to the single-phase powder. The lowest performance was registered for the $\text{LaFeO}_3\text{-La}_2\text{O}_3$ nanocomposites, likely due to the low content of the perovskite in the catalyst and/or to the segregation of inactive La_2O_3 on the surface. Overall, characterization and performance results clearly evidenced limitations and peculiarities of this new approach.

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Keywords : perovskite-type catalysts, solution combustion synthesis, X-ray diffraction, rust wastes, propylene oxidation.

#P043 - Environmental stress tests on transferred CVD Graphene

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Graphene structures, obtained from Chemical Vapor Deposition (CVD) graphene transferred onto an oxidized silicon surface and patterned by photolithography, were aged according to the unbiased environmental test (with high relative humidity and high temperature), that belongs to the standard tests for qualification of microelectronics. Graphene or FLG films are known to be effective as humidity sensors, but until now the effect of a long-term exposure to humidity on a graphene device has been unknown.

Even such a preliminary experiment revealed a complex set of effects on the same batches, ranging from the slight alteration of the relative resistance in otherwise intact devices, to the mechanical destruction of the patterned graphene structure. Before and after the tests, the FLG samples were characterized by optical microscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM); moreover, the changes in the electrical properties of the samples were evaluated using the ratio DR/R_0 .

The results obtained have demonstrated their evident correlation upon mapping their time distribution, as usual for Reliability tests.

The consequence, as will be shown, is the possibility to design life-tests at low-stress levels, identifying in some early changes the precursors for ultimate failures. This means that the resources and potentials of Design for Reliability may be bestowed on an emerging technology, such as the integration of graphene elements into the standard solid-state silicon planar process.

#P044 - Plasmonic Properties of Self-Assembled Au/PNIPAM Core-Shell Nanoparticles Studied with Spectroscopic Ellipsometry

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The ordered assembly of nanoparticles is a key challenge in nanoscience. A convenient approach in this regard is to use self-assembly methods, that allow to create ordered arrays of nanoparticles on a relatively large scale (cm^2) and at a low cost [1]. Such platforms of uniformly-spaced, regularly-shaped nanoparticles can find applications from sensoristics to photovoltaics, provided that their optical response is well understood [2].

Here, we present the spectroscopic ellipsometry (SE) data and analysis of a self-assembled system of core-shell nanoparticles, with gold as a core and the thermoresponsive polymer PNIPAM as a shell. The nanoparticles are arranged on an hexagonal lattice and deposited on glass. The interparticle distance is enough to avoid particle-particle interactions, thus the plasmonic properties of the lattice are dominated by the single-particle response. This Au/PNIPAM system is well suited to investigate the variation in the plasmonic response of Au nanoparticles when surrounded by a dielectric environment (PNIPAM), whose refractive index change with temperature.

For the data analysis and interpretation of the SE spectra, since commonly-used Effective Medium Approximations (EMA) don't provide enough accuracy, we applied a model that explicitly takes into account the key morphological parameters of our system (NPs size, shape, interparticle distance, distance from substrate) [3, 4, 5]. The main spectral feature of the SE data, caused by the plasmonic resonance, is correctly matched by the model. Thus, our approach provides detailed information about the optical properties of this system of nanoparticles, and more in general, it constitutes a flexible tool to investigate 2D arrays of plasmonic particles.

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#P045 - NANOENGINEERED CHIRAL METAMATERIALS FOR BIO-DETECTION

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Chiral metamaterials are an emerging class of metamaterials able to manipulate circular polarized light and they are subject of great interest in the scientific community for many applications. The helical structure allows to obtain a great chiro-optical response when the incident light impacts on it because of a mixture of electric and magnetic dipoles that cause interesting effects as circular dichroism or optical rotatory dispersion. Here we discuss about the possibility to employ 3D plasmonic nanohelix-based metamaterial arrays for high sensitivity biosensing. Devices based on surface plasmon resonances take advantage of the plasmonic resonance peak shift by varying the refractive index of the medium (the biological component to detect) surrounding the plasmonic material. However, although they are widely used, their sensitivity is relatively low especially for small molecules. Chiral metamaterials represent an alternative solution to enhance the sensitivity because circular dichroism has more spectral characteristics than extinction. We perform our work using as a basis the already studied tunable platform based on 3D helical nanostructures, fabricated in an array configuration by means of two techniques: 1) focused ion beam induced deposition (FIBID) and 2) focused electron beam induced deposition (FEBID). This technology demonstrated a strong optical efficiency, together with a high control of the geometrical arrangement allowing operation in a broad spectral range included visible wavelengths. However, the used technology lead to a very complex material and surface system. For example, the composition of FIBID-deposited platinum nanostructures consists of metal nanograins embedded into an amorphous carbon matrix. The complexity of the helical material system and its surface chemistry makes biological applications challenging because of the non-uniform and largely unknown chemical surface structure. To overcome this stumbling block, we employed an alternative functionalization method based on the electrosynthesis of an organic polymer by cyclic voltammetry to obtain an ultra-thin layer of o-phenylenediamine (OPD). The two amino-moieties in the aromatic diamine then enable the binding of bioreceptors/biomolecules. The key point of this methodology is the ability to carry out a conformal deposition of a very thin polymer layer on a complex nanostructure that virtually doesn't interfere with the optical behaviour of the metamaterial and offer an ideal surface for molecular immobilization. By the implementation of this technology and by engineering chiral metamaterials to fully exploit the circular dichroism potentiality, our goal is to obtain enhanced biosensor sensitivity, also for very small molecules.

#P046 - Strain Analysis and Optical Characterization of Strained Silicon Photonics Structures and Waveguides

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Silicon photonics (SiPh) leverages optical, electrical and material properties of silicon with the mature complementary metal-oxide-semiconductor (CMOS) nanofabrication technology to integrate optical devices on microelectronic chips. The weakness of second order (SO) nonlinearities of bulk silicon crystal hindered the development of efficient SiPh devices for frequency conversion and phase modulation that are fundamental functionalities for optical interconnects and switching fabrics*. Nevertheless, the recent discovery of Pockels effect and second-harmonic generation in strained silicon structures has paved the way for the study of nonlinear and active SiPh devices as Mach Zehnder and microrings modulators and switches.

In this work we report the results of a theoretical and experimental study carried out on strained SiPh devices that are deformed by the presence of a stoichiometric silicon nitride (Si_3N_4) film deposited through low pressure chemical vapour deposition (LPCVD). Strain measurements have been carried out employing the transmission electron microscope (TEM)-based convergent beam electron diffraction (CBED) technique. CBED allows for <10 nm spatial resolution and strain sensitivity of 100 $\mu\epsilon$. Furthermore, we have developed a finite element method (FEM)-based simulative multi-physical model to evaluate the spatial distribution of the strain tensor and the deformation-induced electromagnetic properties of the SiPh devices. Then we have performed a comparative analysis of CBED outcomes with the simulative results: both analyses yielded maxima values for shear and normal stress of the order of $m\epsilon$ for micrometric and nanometric structures. The quantitative agreement among the experimental and simulative analysis allowed us to validate both the CBED technique, that had never been employed for the analysis of deformed silicon structures, and the developed multi-physical model that we have used to evaluate the optical properties of the strained SiPh waveguides as a function of Si_3N_4 stressor film thickness. In particular, modal intensity distribution, effective refractive index and birefringence behaviours have been simulated for Si_3N_4 thickness values up to 450 nm.

The analyzed SiPh structures and devices have been manufactured using the spacer patterning technique that allowed us to realize nanowires with dimension < 450 nm and distanced by < 300 nm wide gaps using a photolithographic system that has a minimum feature size of 700 nm. The employment of this technique for the manufacturing of SiPh devices represents a novelty: in order to evaluate and validate the quality of the manufacturing process, TEM analysis and propagation loss measurements have been performed on the nanofabricated structures.

#P047 - Growths and characterizations of n-type epsilon-Ga₂O₃ doped films

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Gallium oxide (Ga₂O₃) is a semiconducting material with wide bandgap of 4,7-4,9 eV, of great interest for different applications in the area of power electronics, solar blind UV photodetectors, solar cells, and sensors¹. Our research group is mostly involved in the preparation of the ε-Ga₂O₃ polymorph by Metal-Organic Vapor Phase Epitaxy (MOVPE). Single-phase epilayers were deposited on c-oriented sapphire substrates at a temperature of 600-610 °C and total reactor pressure of 60 mbar. As precursor gases, Trimethylgallium (TMG) and ultrapure water, with an oxygen/gallium partial pressures ratio in the range of (100÷200), were used. These reagents are stored in dedicated stainless steel bubblers kept at 1 °C and 30 °C, respectively, and ultrapure H₂ is used as carrier gas, with a flow of 2000 sccm. We present here, for the first time, the n-type doping of the layers, obtained using SiH₄. To this extent, diluted (0,05%) silane in H₂ was injected into the growth chamber through the TMG precursor line. As-deposited Ti-Au ohmic contacts, made by RF-sputtering, on the corners of 5mm × 5mm square samples exhibited a nearly ohmic behaviour in a relatively wide range of their I-V characteristics. Hall measurements were then carried out in van der Pauw configuration. The Hall voltage was seen to be weakly dependent on the temperature, and Hall mobilities of a few cm²/Vs and carrier densities of the order of 10¹⁸ cm⁻³ were measured. The electrical measurements were performed in vacuum under dark conditions, in the (10÷600) K temperature range, first lowering the temperature from RT to 10 K and then increasing it up to 600 K. The lowest resistivity was about 0.5 Ωcm. The plot of resistivity vs. T^{-1/4} is linear, which strongly suggests that conduction takes place via hopping between localized states (impurity band conduction). Nonetheless, the resistivity of these doped layers dropped by several orders of magnitude with respect to nominally-undoped ε-Ga₂O₃, which opens the way to novel device fabrication.

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#P048 - ADDITIVE MANUFACTURING OF MINIATURE COMBUSTORS

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Additive manufacturing allows producing three-dimensional components, layer by layer, directly from the mathematical model of the object. It includes a large family of technologies each of them dedicated to a single material (metal, plastic, concrete,...), even if hybrid equipments are also available. In this work, Fused Deposition Modeling (FDM) and Selective Laser Melting (SLM) technologies are implemented in order to produce a Thermoelectric Generator (TEG) which consists of a miniature combustor prototype coupled to thermoelectric modules. The combustor is composed by a hexagonal hollow prism cell with 18x18mm² lateral surface and 2mm thickness walls whose inner surfaces present pins to improve thermal flow during the combustion. Cylindrical Alumina pellets (3.2 mm diameter and 3 mm high) covered with a thin layer of Platinum catalyzer are orderly placed at the bottom of the cell. The cell is hermetically closed by a cap that presents two grafts, one for the inlet of the combustion gases and the other for the outlet of the exhausts. The cap is shaped to force the gas through the pellets and along the cell walls promoting a uniform distribution of temperature.

Pre-prototypes were realized by a Stratasys Dimension Elite FDM machine that works with a plastic ABSplus filament which is unwound from a coil and continuously supplied to produce the part layer-by-layer. The device was finally processed in Argon atmosphere by a Renishaw AM400 SLM machine with fine gas-atomized SS316L micrometric powder. Before the supports removal, thermal treatment in air atmosphere at 450°C for 2 hours has been performed to relieve the stresses generated during the process (cooling was done in furnace). Finally, the parts have been removed from the building plate and post processed to refine the surfaces.

Preliminary combustion tests have been carried out in order to prove the mechanical stability of the device. Moreover, two-dimensional distribution of temperature measurements have been collected on external combustor walls by using a thermocamera and a reasonable

uniformity of temperature through the surfaces has been obtained. Finally, as upgrades of the device, FDM was used to produce plastic heat exchangers designed to extract heat from the combustor walls.

#P049 - Selective fabrication of photo-luminescent Quantum Dots by laser patterning

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The work presents the preliminary outcomes related to the selective generation of CdS QDs in a polymeric film by using tightly focused UV laser. The activities are in the frame of the H2020 MiLEDI project (www.miledi-h2020.eu) with the final aim to fabricate an innovative display obtained combining a blue LED matrix with an active light-converter polymeric film.

Two types of precursors based on cadmium xanthates are used to dope PMMA film. These films are then patterned by UV laser source in different conditions, the generation of photo-luminescent QDs is then observed by a multi-channel confocal microscope. These photo-luminescence are not obtainable by oven treatment confirming the role of photo-chemical phenomena in the activation of QDs.

QDs emission is strictly related to the adopted laser parameters and the different precursors behave in different ways illuminated by high intensity UV pulses even if their absorption spectrum is similar.

The second interesting result is that the effect of the laser is the production of luminescent pattern only for certain fluences and that the same film treated with the temperature did not show any luminescence.

These results point out the role of the laser light in the process of luminescent QDs growth that the temperature can't activate.

#P050 - Thermodynamics and kinetics of hydrogen sorption below 150 °C in MgH₂-TiH₂ composite nanoparticles

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The hydrogen sorption properties of Mg-based nanostructures have been the subject of extensive research in the past decade. While it is understood that both thermodynamics and kinetics may be affected by features such as interface free energy, elastic strains, and shorter diffusion distances, most experiments were carried out at temperatures around 300 °C where Mg-based nanomaterials are highly unstable [1]. Equilibrium and kinetic data at low temperature have eluded experimental observations. The present work is a breakthrough in this respect because both the equilibrium pressure and the kinetics of hydrogen absorption and desorption have been measured between 100 and 150 °C [2]. The materials under study are MgH₂-TiH₂ composite nanoparticles (10-20 nm in diameter) obtained by reactive gas-phase condensation of mixed Mg-Ti vapors in a He-H₂ atmosphere. To minimize spurious effects due to surface contamination, the nanoparticles have been characterized *in situ* in the ultra-high-vacuum synthesis chamber by a combination of Sievert manometry and thermal desorption spectroscopy. We report the modeling of hydrogen sorption kinetics, the pressure-composition isotherms and the thermodynamic parameters, i.e. enthalpy and entropy of hydride formation, as a function of Ti content [2,3]. The influence of MgH₂/TiH₂ interfaces on both thermodynamics and kinetics is discussed.

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#P051 - Recombinant mussel protein Pvfp-5β: a potential tissue bioadhesive

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Many marine organisms rely on natural adhesives to attach to various surfaces in wet conditions for their life-cycle, movement and self-defense in aqueous tidal environments. Mussel adhesive proteins have received increased attention in recent years for their potential applications in several fields, such as medicine, bioscience and biotechnology being biocompatible and able to elicit minimal immune response. The Asian green mussel *Perna viridis* secretes several byssal plaque proteins and the *Perna viridis* foot protein-5β (Pvfp-5β) is the first protein to initiate interaction with the substrate, displacing interfacial water molecules before binding to the surface (1). Here, we present a study focused on recombinant Pvfp-5β, considered as a key adhesive material. After the expression and purification of the recombinant protein from *E. coli*, we evaluated both its effect on cell viability and cell adhesive capacity using NIH-3T3 and HeLa cell lines. Our results revealed that the protein has no cytotoxic effect at the investigated protein concentrations and shows a good cell adhesion strength on both glass and plastic plates. Circular Dichroism spectra and Dynamic Light Scattering measurements allowed

elucidating the secondary structure and aggregation properties of recombinant Pvfp-5bin aqueous solution. Overall our results show that the adhesive properties of recombinant Pvfp-5 β make it an efficient surface coating material, suitable for several biomedical applications including the regeneration of many types of damaged tissues.

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#P052 - WO₃/BiVO₄ photoanodes for photoelectrochemical water splitting: a high resolution X-ray spectroscopy investigation

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WO₃/BiVO₄ thin films are among the most studied photoanodes for photoelectrochemical (PEC) water splitting. Further improvement of BiVO₄-based devices depends on a deeper understanding of the dynamics of photo-generated electrons and holes to identify the factors that presently limit the Solar to Hydrogen (STH) Conversion Efficiency. High energy resolution fluorescence detected (HERFD)-XANES is a very powerful tool to determine the local structure of advanced materials, with the additional possibility of performing experiments under differential illumination and/or operando conditions [1, 2, 3, 4]. We will describe and discuss a recent HERFD-XANES experiment at V K-, Bi L₃- and W L₃-edges performed at the ID26 beamline of the ESRF. The measurements were performed with a specially designed PEC cell which permits operando XANES measurements. In order to obtain a greater insight into the system, the x-ray spectroscopic measurements were performed at the same time as PEC water splitting, the applied anodic voltage being used to tune charge separation and hole transfer rate at the photoanode/electrolyte interface.

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#P053 - Compounds with high added value derived from marine by-products

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The valorisation of by-products from food industry is important both to reduce the waste discharged in the environment, and to produce valuable chemical compounds from a renewable source.

In this work we report the use of by-products of the fish industry for the extraction/production of compounds with high added value, usable in biomedicine. The considered by-products included seashells and bones from different fishes.

Calcium phosphate-based powders were obtained from these sources with a simple thermal extraction process and/or with a low temperature chemical conversion. A full characterisation of these materials was performed, to produce the materials with the best composition and physical features. Some selected samples were then employed to make 3D scaffold structures, usable as bone substitute.

This study showed the potential of food by-products to obtain bioactive compounds, with high interesting biomedical applications.

#P054 - Rylenediimide derivatives as a new molecular platform for n-type WG-OFETs: the role of thin-film growth modality in engineering the electrolyte-semiconductor interface

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The Water-Gated Organic Field-Effect Transistor (WGOFET) is one of the most promising device architecture for stimulating and recording cell electrophysiological activity given the possibility of biofunctionalization of the organic/electrolyte interface [1]. Here we present for the first time the use of two electron-transporting PDI derivatives, named PDIF-CN₂ and PDI8-CN₂ [2], as active materials in WGOFETs. The two materials have an identical solid-state arrangement but show two different growth mechanisms: almost-2D layer-by-layer for PDIF-CN₂ and 3D for PDI8-CN₂. The electron mobility of PDI8-CN₂ shows a saturation with increasing the semiconductor layer thickness ($\sim 10^{-4}$ cm²/Vs at 10-15 nm layer thickness). Differently from other semiconductors used in WGOFETs, whose mobility saturates after 1-2 monolayers from the semiconductor/water interface, the PDIF-CN₂ mobility increases unexpectedly with the semiconductor film thickness up to 35 nm while preserving an almost-2D growth modality. The achieved mobility values are comparable to state-of-the-art p-type semiconductors ($\sim 10^{-3}$ cm²/Vs). Cross-correlated experiments and theoretical evidences suggest that crystallinity and end-substituents (fluorinated-chain for PDIF-CN₂ and alkyl-chain for PDI8-CN₂) are not the major causes of the more performing electrical characteristics of PDIF-CN₂-based WGOFET. Features of semiconductor/water interface are found to be dependent on the overall film thickness for PDI8-CN₂ while no change is observed for PDIF-CN₂ until the almost-2D growth modality is preserved. Upon these experimental results, we can suggest that the charge-mobility increase in PDIF-CN₂ is likely correlated to a bulk-conduction contribution to the field-effect charge transport. Moreover, the electron-rich end-substituents of PDIF-CN₂ organize into an ordered and dense interlayer at the semiconductor/electrolyte interface, which increases the surface hydrophilicity while avoiding water molecules percolation. These insights may enable the definition of a new material paradigm for the realization of performing WGOFETs for use in biological signal transduction.

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#P055 - Ordered arrays of silver nanodots on transparent conducting substrates

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Plasmonic properties of silver nanostructures can be exploited to enhance the ultraviolet performance of silicon drift photodetectors and photovoltaic devices by improving the electrical signal consequent to increased optical absorption at high energy (3 eV and higher).

The study of the optical properties, as well as the setting up of the required technology, involves the investigation on the intermediate fabrication steps.

One way to fabricate the silver nanodots is by deposition through a nanostructured ordered template. In this contribution, silver nanodots are fabricated by thermal evaporation of silver through separately fabricated porous alumina membranes. Different patterns are obtained using membranes with varying pore diameters, pitches and thicknesses, previously transferred on Indium-Tin-Oxide (ITO) layers on transparent substrates.

The optical characterization by means of Reflectance and Transmittance spectroscopy shows the Localized Surface Plasmon (LSP) resonance of the silver nanodots pattern. Results are simulated by means of the Generalized Transfer Matrix method. The properties of silver nanostructures are simulated by making use of the Lorentz oscillator model associated to free carrier absorption (FCA) formalism. FCA parameters are tuned on the specific collision frequency related to the nanodot diameter. The LSP resonance is simulated by means of an additional Lorentz oscillator. The characterization allows for direct monitoring of the fabrication process parameters.

#P056 - Investigation of graphene contacts on Ge₂Sb₂Te₅ layers for application in phase-change memory devices

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The possibility to replace the metal contacts in phase-change memory (PCM) devices with a 2D nanomaterial such as graphene (G) has been already investigated in the literature. However, the fabrication of reliable and robust G contacts on Ge₂Sb₂Te₅ (GST) material is still an issue. The role played by leads and contacts in aggressively-scaled memories is of the utmost importance: in order to achieve an efficient increase in the memory density, it is necessary to match the shrinkage of the single memory cell with the scaling of the metal connections paths.

In the present work, we discuss some mechanical, physical and electrical properties of a CVD-grown graphene layer transferred on 50 nm-thick Ge₂Sb₂Te₅ chalcogenide for application in PCM devices. The extensive investigation carried out on the G / GST interface by means of Electron Energy Loss Spectrometry (EELS), Raman spectroscopy and Transmission Electron Microscopy (TEM) showed

the expected chemical composition at the interface, no bond distortions in the chalcogenide layer after graphene transfer and the presence of defects in the overlying graphene layer.

We evaluated the quality of the contact stack by measuring the adhesion of G on GST layer using the scratch test analysis and the sheet resistance measurements of the layers themselves. The main key aspects for the fabrication of reliable and robust contacts on GST turned out to be the mechanical adhesion of G on GST and the low sheet resistance of the G layer. Scratch tests revealed a stress distribution compatible with a failure of the interface where the graphene layer features a 2 %-void. The contact showed an effective good Ohmic quality, but in some samples the G sheet resistance was too high, up to 1000-1400 Ohm/square. In the case of nano-scaled G contacts and line or bridge-like structures (with laterally arranged contacts), a high contrast between the G and GST sheet resistances is desirable, for avoiding significant leakages through the GST film, that may exceed the in-plane conduction in the G contact. For this reason, in order to improve the G/GST contact, we investigated both alternative G layer transfer techniques (reaching sheet resistances down to $360 \div 380$ ohm/square), with an accurate control of the sheet quality (continuity, presence of defects, number of layers) and the use of G doping techniques before transfer on the GST layer.

#P057 - Hexanal sensing properties of pure and iron-doped electrospun zinc oxide fibres

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Although hexanal ($C_6H_{12}O$), one of the major volatile compound released during food storage due to lipids oxidation, is an important food quality marker in packaging [1], its detection has not been extensively studied yet. Up to date, only tin oxide [2] and chitosan-polyvinyl alcohol [3] resistive sensors have been proposed, but sensitivity and response time still represent the main concerns. The development of effective commercial sensors calls for the development of new sensing materials. A recent study has highlighted the great potential of zinc oxide, a low cost, non-toxic semiconductor [4].

This contribution deals with the synthesis of pure and iron-doped zinc oxide (ZnO and $ZnO:Fe$) nanofibres (NFs), the fabrication of resistive sensors by using the NFs as an active material, and the evaluation of their performance in the hexanal sensing.

ZnO and $ZnO:Fe$ NFs were prepared by electrospinning of solutions with different Fe:Zn loading ratios (0:100, 1:40 and 1:20), followed by calcination in air at 600°C for 2 h.

The analysis of the so-obtained ZnO -based NFs by means of complementary techniques evidences that the variation of the Fe:Zn loading ratio produced no significant changes in the NF morphology. Both the highly porous ZnO and $ZnO:Fe$ NFs consist of interconnected grains of oxide with the hexagonal wurtzite structure of zincite. No evidence for the segregation of iron in secondary phases is found. The elemental mapping proves that dispersion of zinc, oxygen and iron within the NFs is spatially uniform.

In order to assess their performance in the detection of $C_6H_{12}O$, sensing devices were fabricated as previously described [5], using the electrospun ZnO and $ZnO:Fe$ NFs as an active material. Sensing tests were operated at different temperatures (200, 250 and 300°C) by measuring the response to small concentrations of hexanal in air (6–35 ppm).

The preliminary results show that $ZnO:Fe$ NFs exhibit good linearity and improved sensing performance with respect to ZnO NFs; 250°C and 1:20 appear to be the optimal sensor operating temperature and the optimal Fe:Zn loading ratio, respectively. Measured recovery times are much lower than those previously reported in the literature [5].

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#P058 - From regular to spherical sol-gel gold catalyst

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The oxidation of alcohols to aldehydes with O_2 in place of stoichiometric oxygen donors is a crucial process for the green synthesis of fine chemicals, as well as important from the environmental point of view are solvent-free reactions. The final goal is the synthesis of fine chemicals under mild reaction conditions with little or no waste generation, using catalytic processes in which the solid catalyst can be easily separated at the end of the reaction and recycled or even better, used in continuous processes as in flow microreactors.

Sol-gel ORMOSIL (organically modified silica) entrapping gold nanoparticles, have been successfully employed in the solvent-free selective oxidation of alcohols to aldehydes with low pressure O₂ as primary oxidant (Ciriminna et al. *ChemCatChem* 2017, 9, 1322). The catalysts are truly recyclable being reusable in different consecutively runs with only slight decrease of the activity.

In order to further improve the performance of gold on hybrid silica, we have developed a new catalytic material by deposition of gold nanoparticles on sol-gel spherical silica. Preliminary catalytic test on spherical gold catalysts to be presented at the Materials.it 2018 conference will show the significant impact of geometry and shape on the catalytic activity.

#P059 - Titanium biofunctionalization with Self Assembling Peptides and Chitosans: SR-XPS study

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Titanium is a biocompatible material widely used in medicine for the preparation of orthopedic/dental prostheses, thanks to its well known ability to promote osteointegration. Recently, a great research effort was devoted to the development of bioactive coatings on titanium implants, with the aim of obtaining engineered biomaterials most appropriate for long-term treatment of critical-sized bone defects. The quest for developing the most suitable bioactive prosthetic surface has been addressed from different perspectives: the composition of the bioactive material, the structure of the coating, the surface topography features, and the fabrication techniques used to prepare the desirable coating. However, bacterial infection following surgical implantation of biomaterials and devices poses a risk to implant successful osteointegration. Recently, it was shown that, among the different bioactive inorganic materials investigated, Ti surfaces functionalized with chitosan molecules are able to prevent bacterial adhesion through a mechanism involving the interaction between the oppositely charged bacterial cell wall and the chitosan. This interaction results in a change in bacterial membrane permeability, leading to the fatal leakage of cellular contents. Chitosan is a polysaccharide formed by D-glucosamine monomers and can be functionalized through the amino group, by reaction with organic molecules, introducing a pending group with the desired properties in the polysaccharide backbone. In the past, we have studied the immobilization on the titanium surface of selected peptide sequences aimed at promoting osteoblast adhesion and therefore bone growth. We extend our study to surface functionalization with chitosan molecules having anti-bacterial properties. The final goal is to obtain titanium surfaces capable to prevent bacterial adhesion and promote osteoblast adhesion at the same time. The design of an orthopaedic prostheses, destined to a biological environment, must depend on the knowledge of the composition of the surface and the stability of the material. In fact, the specific nature of a material's surface, both chemically and physically, determines how the organism interacts with the implant. SR-XPS is extremely well suited to investigate the chemical and molecular structure of small molecules adsorbed or covalently grafted to surfaces and gives fundamental information for the development of new functionalized materials for biomedical application. We investigate the chemical, electronic, molecular structure at the surface of chitosan/Ti and "modified chitosan"/Ti scaffolds, in order to select, among a series of proposed composite materials, the best candidates as bioactive material for osteointegration.

#P060 - BODIPY DYES AS PROMISING MATERIALS FOR STRONGLY COUPLED MICROCAVITIES

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4,4-Difluoro-4-borata-3a-azonia-4a-aza-s-indacene dyes, more commonly known as BODIPY dyes, have been long since recognized for their excellent optical properties such as high absorption coefficients, high fluorescence quantum yields, and remarkable photostability¹. Discovered for the first time in 1968 by Treibs and Kreuz², BODIPY dyes are of wide importance and have a broad use as laser dyes in biological sensing, organic electronic, and other possible applications³.

Recently BODIPY molecules dispersed in a polymeric matrix like polystyrene (PS) have been also used to achieve polariton condensation in strongly coupled microcavities⁴.

Here we present the synthesis, photophysical and gain properties of a series of BODIPY dyes functionalized with lateral substituents to improve their film forming ability and to reduce the effect of PL quenching. This will permit such dyes to be used at high concentration in a strongly coupled microcavity and will allow to reduce the threshold for polariton condensation.

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#P061 - Battery-free fully integrated microfluidic light source for portable lab-on-a-chip applications*Filippo Storti - Istituto Italiano di Tecnologia**Other Authors: Silvio Bonfadini (Istituto Italiano di Tecnologia), Luigino Criante (Istituto Italiano di Tecnologia)*

Integrating a light source inside a Lab on a Chip platform has always been a challenging as much as appealing task. Besides the manufacturing issues, one of the most limiting aspects is due to the need of an energy source to feed the light emission.

Chemiluminescence (CL) is a well-known chemical phenomenon in which flash-type light emission is achieved as consequence of a chemical reaction. This peculiar “light system” has found its widespread use in detection assays, especially in the biological samples analysis. Some works, though, demonstrated the validity of CL as a light source, coupling it with photoelectrochemical method. However, these works still present few limits, related to macroscopic scale systems, that Microfluidics aims to overcome.

Here we present the fabrication and the characterization of a chemiluminescent light source, fully integrated on a microfluidic platform by means of the direct writing technique known as Femtosecond Laser Micromachining. The key advantage is the possibility to insert within Lab-On-a-Chip (LOC) devices incoherent light sources with complete freedom of space positioning and wide flexibility of the emitting source geometry. Furthermore, by combining one of the intrinsic Microfluidics characteristics - i.e. to process small volumes - with the use of a chemical reaction, it was possible to extend the reaction emission time for a few hours.

The characterization was carried out by investigating the effect of confining a chemiluminescent Rubrene-based reaction in small volumes and the inject pressures impact on the emission spectra.

#P062 - Optical investigations on Yb³⁺/Er³⁺/Tm³⁺ doped PZT phosphor for the application in forensic fingerprint detection & bio-imaging*Prasenjit Prasad Sukul - In**Other Authors: Dr. Kaushal Kumar Indian Institute of Technology (Indian School of Mines), Dhanbad*

Herein, the energy up conversion emission studies on solid state route prepared PbZrTiO₃:Yb³⁺/Er³⁺ phosphor for the application in forensic fingerprint detection & bio imaging has been done. The up conversion emission of PZT:Yb³⁺/Er³⁺ phosphor has been recorded using 980 nm laser excitation with various temperature treatment. The upconversion (UC) emission intensity ratio of green to red bands is found too high to neglect the contribution from the red emission band, which is not observed normally in Yb³⁺/Er³⁺ doped materials under the exposure of 980 nm wavelength excitation. An observed comparison between UV vs. NIR excited fingerprint images shows that fingerprint images exposed by NIR excitation have more clear edges than the UV excitation. Hence upconversion emission of in Yb³⁺/Er³⁺ doped PZT phosphor is preferred by the authors for the application in fingerprint detection which has a great importance in forensic data science. The emission dynamics is studied with respect to its dependence on input power and external temperature including lifetime. Furthermore, the present phosphor could be useful for bio-imaging regime. The 808 nm wavelength excitation produces lesser heating in a biological medium compared to the 980 nm excitation and hence in this regard Er³⁺ can be a good option for transparency across 2nd biological window. UC/DC emission in “NIR biological windows” has less absorption in biological medium and hence can be imaged easily.

#P063 - Optical properties of nanostructured gold films on free standing sodium alginate membranes*Caterina Summante - CNR-IMM**Other Authors: P. Maccagnani, A. Desalvo, L. Ortolani, G. Pizzochero (CNR-IMM UOS Bologna, Bologna, Italy); R. Capelli (CNR-IOM AREA Science Park, Basovizza, Trieste, Italy); M. Bertoldo (CNR-IPCF UOS Pisa, Pisa, Italy); F. Dinelli (CNR-INO, Pisa - S. Cataldo, Pisa, Italy).*

Gold thin films have been fabricated by magnetron sputtering on free standing sodium alginate membranes. The material finds its interest in biomedical and wearable applications, where the use on non-conventional, disposable, and biocompatible substrates represents an added value to the technology.

The material has been characterized by means of UV-visible Reflectance & Transmittance (R&T) spectroscopy in combination with optical simulation, and by Scanning Electron Microscopy associated to Focussed Ion Beam sample preparation. Optical simulation of R&T spectra was carried out by making use of the Generalized Transfer Matrix Method, associated to the Bruggeman Effective Medium approximation to take into account the void fraction.

The optical properties of the gold films were analytically fitted by means of the Lorentz-Drude model, further improved by the introduction of the signal of the Localized Surface Plasmon, which was simulated by the introduction of a specific oscillator in addition to those related to bulk gold. Moreover, the simulation implied taking into account the dependence of the mean free path on nanoparticle size, and the related modification of the Drude term in the definition of the dielectric constant of the material.

The results indicate the initial formation of a nanostructured, low density material associated to a fairly high deposition rate. As the deposition proceeds, the material evolves toward a continuous, more dense film, with an apparent decrease of the deposition rate, although the atomic deposition rate remains constant. The results are corroborated by SEM observations. The formation of a continuous film is associated to the disappearance of the LSP signal, and to the reduction of the collision frequency to the value of bulk gold. The results show the capabilities of UV-visible R&T spectroscopy to describe the structural evolution of the material, and to put in evidence its optical and electronic peculiarities.

#P064 - Raman microscopy analysis of graphene-based nanocomposite materials under UV-C exposure

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In this work, we focused on the investigation of UV-C radiation effects on novel nanomaterials structured with graphene nanoplatelets (GNPs) and DNA. Multifunctional nanocomposites were realized by combining the good electrical conductivity of GNPs with the biocompatibility and UV sensitivity of double-stranded DNA. GNP/DNA nanostructures were prepared by sonication-driven self-assembly in aqueous solution, and then dispersed into a PEDOT:PSS (poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)) matrix. The UV-sensitivity of the GNP/DNA/PEDOT:PSS samples was investigated by exposing them to the energetic UV-C band, and investigating their morphology, surface wettability, chemical and electrical properties before and after irradiation using several techniques (scanning electron microscopy, Raman spectroscopy, electrical impedance spectroscopy). In particular, Raman imaging was used as suitable technique to analyze the chemical arrangements and their modifications upon irradiation on selected surface areas. This technique allowed appreciating chemical changes caused by the UV-C interaction with the nanocomposite original structure. Results give information about the potential applications of GNP/DNA/PEDOT:PSS nanomaterials in all environments affected by UV radiations, for example for chemical reactions or sterilization purposes, or where they are naturally present, such as in space. In reference to space environment, the GNP/DNA/PEDOT:PSS nanocomposites were also tested under UV-C while reducing the amount of oxygen reaching the sample surface, in order to separate the effects due to the atmosphere from those of the irradiation.

#P065 - Functionalization of phosphorene by pyrene based chromophores

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2D materials have attracted great interest in a variety of applications due to materials' anisotropy, chemical reactivity and thickness-dependent properties. Among them, black phosphorus (BP) has recently gained great attention due to its unique electronic and optical properties. The size depended band gap can vary from 0.3 eV for bulk BP to 2 eV for the single layer, namely phosphorene, prepared by exfoliation of BP. This form, which structurally resembles graphene, represents an intriguing material for electronic and optical applications and as replacement for semiconductors in computer circuits.¹ However, the high water and air sensitivity represent a great drawback for its widespread use. Several strategies on exfoliation and coating procedures to improve its stabilization against oxidation have been developed² while few works deal on chemical reactivity and functionalization processes. A covalent C- P bond has been formed between aryl diazonium salts and phosphorene³ and non-covalent interactions have been found to occur with aromatic compounds.^{4,5} Here we report on a functionalization study of phosphorene by organic luminescent dyes based on pyrene core, bearing boronic functionalities. Pyrene 1- boronic acid (PBA), 4,4,5,5- tetramethyl- 2-pyren-1-yl-1,3,2- dioxaborolane (PBE) and pyrene (PY) have been examined. Spectroscopic investigations have showed a change of time resolved properties of the chromophores, i. e. the increase of fluorescence lifetime and of rotational correlation time, thus indicating the occurrence of an interaction between pyrenes and phosphorene. This work provides new insights on chemical properties of phosphorene, opening the way to a new functionalization strategy of the material by organic luminescent dyes. For example, due to the excellent optical response of pyrene, surface analysis of the material can be carried out, i. e. identification of superficial defects whose determination is important for the use of phosphorene in electronic devices.

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#P066 - Study of 2D supramolecular self-assembled layers of phenyleneethynylene oligomers on HOPG by scanning tunneling microscopy

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The type of supramolecular organization of conjugated macromolecules in solid state is an important feature to be considered for the optimization of optoelectronic properties of active layers for solar cells. We report on the scanning tunneling microscopy (STM) and small-wide angle X-ray scattering (SWAXS) study of four linear and rigid π -conjugated p-phenyleneethynylene (PPE) oligomers. The four compounds possess two dodecanoxy side chains in the central PPE moiety, and differ in conjugation length (3 and 5 phenyleneethynylene moieties). Two oligomers are benzyl (**Bz3PEBz**, **Bz5PEBz**) and two are carboxylic acid groups (**Ac3PEAc**, **Ac5PEAc**) end-capped. We found that in carboxylic acids terminated oligomers, a lineal type arrangement is obtained, likely due to the hydrogen bridge created between carboxylic acids; in contrast, for the benzylbenzoate terminated oligomers a rather step-wise arrangement is obtained, promoted by the π - π interaction between benzyls. In general, all of the molecules form a lamellar like pattern adopting a face-on arrangement, where the conjugated backbones are flat-lying on the HOPG surface, whose distances correspond to the length of the conjugated backbone, while within the lamellas, a distance of 1.52 nm corresponds to the space between conjugated backbones; values that are consistent with those found by WAXS and DFT/6-311G(d,p) theoretical calculations, for oligomers that self-assemble with the interdigitated lateral alkyl chains.

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#P067 - Perpendicular magnetized GMR spin valves with a synthetic antiferromagnetic reference layer on flexible substrates

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Flexible electronics has received a great deal of attention over the past decades owing to its outstanding potential in many technological fields including energy, optics, sensors and information storage, among others [1,2]. Flexible devices provide wide advantages over their conventional rigid-substrate counterparts, such as the ability to bend and adjust the shape of a device, a lower weight and lower costs.

To expand the domain of flexible electronics, a significant effort has been recently pursued to develop spin-related electronic devices on flexible substrates [2]. In this work, we investigated the possibility to obtain high-quality GMR heterostructures with perpendicular magnetic anisotropy on flexible substrates by exploiting a *transfer-and-bond* approach where the heterostructure is first deposited on a rigid substrate covered with a weakly-adhering layer, and then transferred on an adhesive and flexible substrate by a simple mechanical peel-off step, similar in nature to the methods used for the exfoliation of graphene and other materials. For this purpose, a 10-nm Au layer was first deposited by DC-sputtering onto a thermally oxidized Si substrate due to the low adhesion coefficient of Au on such a substrate. On top of the Au layer, $[\text{Co/Pd}]_4/\text{Ru}/[\text{Co/Pd}]_4/\text{Cu}(x \text{ nm})/[\text{Co/Pd}]_2$ GMR stacks ($x = 2$ and 5 nm) with a fully compensated $[\text{Co/Pd}]_4/\text{Ru}/[\text{Co/Pd}]_4$ synthetic antiferromagnetic reference layer were deposited at room temperature and the magnetic and magneto-transport properties were investigated as a function of the Cu spacer thickness. The same GMR stacks were also directly deposited on thermally oxidized Si substrates as comparison. All the samples present a clear perpendicular anisotropy even when deposited on the Au layer. The Au-free reference samples show the expected field-dependent magnetization response, the GMR ratio assuming a maximum value of about 5% for a Cu thickness of 2 nm. When the stack is deposited on Au, a worsening of the magnetic properties is observed when a thin Cu layer is used, likely because of the presence of exchange interactions between the reference and free layers induced by the rougher Au interface. However, for thicker Cu spacers, the magnetic properties are maintained and a GMR ratio of about 2% is achieved. Such a stack was successfully transferred on an adhesive tape, thus confirming that the proposed transfer-and-bond approach can be pursued to obtain complex spintronic heterostructures on flexible substrates.

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Chowdhury Debasree	#052	Materials and Modelling for Energy Conversion
Christian Meganne	#099	2D Materials for Energy and Environmental Applications
Christian Meganne	#124	Growth and Synthesis of 2D Materials
Christian Meganne	#256	Materials and Technologies for Energy Storage
Ciavatti Andrea	#177	Organic/Hybrid and Printed Electronics and Photonics
Conte Sonia	#026	Cultural Heritage
Corrà Stefano	#064	Molecular self-assembly and supramolecular materials
Cortese Barbara	#160	Stimuli Responsive Bioorganic Materials and Smart Surfaces
Cramer Tobias	#228	Electronic and Photonic Devices for Biological Applications
Cuoco Mario	#189	Topology and Electronic Correlation in Magnetism and Superconductivity
Cuscunà Massimo	#215	Metamaterials, Plasmonics and Nanophotonic systems
D'Addato Sergio	#021	Metamaterials, Plasmonics and Nanophotonic systems
D'Amico Pino	#234	First Principles Modelling of 2D Materials and their Heterostructures

Da Como Enrico	#035	Photophysical and Non-linear Phenomena
Daldosso Nicola	#185	Nanobiocomposites for In-vitro Diagnostics and Targeted Drugs
De Giorgi Milena	#217	Metamaterials, Plasmonics and Nanophotonic systems
De Marco Luisa	#019	Metamaterials, Plasmonics and Nanophotonic systems
Decataldo Francesco	#231	Electronic and Photonic Devices for Biological Applications
Di Carlo Gabriella	#022	Cultural Heritage
Di Mauro Alessandro	#111	Materials and Processes for Environment Protection and Sustainability
Donarelli Maurizio	#167	Advanced Structural Characterization of 2D Materials
Fanciulli Carlo	#001	Materials and Modelling for Energy Conversion
Fatti Giulio	#101	2D Materials for Energy and Environmental Applications
Fazio Maria Antonietta	#104	Materials and Processing for Energy
Ferrari Laura	#159	Stimuli Responsive Bioorganic Materials and Smart Surfaces
Ferri Fabio	#012	Colloidal particles and nanoparticles
Fiorenza Patrick	#198	Advanced Nanofabrication and Characterization of Electronic and Photonic Devices
Fittipaldi Maria	#147	Low-dimensional Structures for Nanoelectronics and Nanophotonics
Focarete Maria Letizia	#155	Stimuli Responsive Bioorganic Materials and Smart Surfaces
Fraboni Beatrice	#224	Electronic and Photonic Devices for Biological Applications
Fratelli Ilaria	#072	Organic/Hybrid and Printed Electronics and Photonics
Fratesi Guido	#092	Molecular self-assembly and self-organized nano and mesostructures
Freddi Sonia	#225	Electronic and Photonic Devices for Biological Applications
Freddi Sonia	#141	Low-dimensional Structures for Nanoelectronics and Nanophotonics
Galassi Carmen	#196	Advanced Nanofabrication and Characterization of Electronic and Photonic Devices
Galizia Pietro	#057	Materials and Processes for Environment Protection and Sustainability
Gentilini Silvia	#070	Organic/Hybrid and Printed Electronics and Photonics
Giannini Cinzia	#042	Computational and experimental methods for soft matter
Giansante Carlo	#010	Colloidal particles and nanoparticles
Giordani Martina	#227	Electronic and Photonic Devices for Biological Applications
Giorgio Michele	#222	Advanced Nanofabrication and Characterization of Electronic and Photonic Devices
Giovanella Umberto	#201	Organic/Hybrid and Printed Electronics and Photonics
Giuri Antonella	#175	Organic/Hybrid and Printed Electronics and Photonics
Giuri Demetra	#066	Molecular self-assembly and supramolecular materials
Gondolini Angela	#005	Materials and Modelling for Energy Conversion
Gori Alessandro	#067	Molecular self-assembly and supramolecular materials
Gradone Alessandro	#053	Materials and Modelling for Energy Conversion
Grasselli Federico	#142	Low-dimensional Structures for Nanoelectronics and Nanophotonics
Grasselli Federico	#047	Computational and experimental methods for soft matter
Groppi Jessica	#136	Stimuli-responsive materials
Guandalini Alberto	#245	Low-dimensional Structures for Nanoelectronics and Nanophotonics
Guarino Vincenzo	#115	Biomaterials for Regenerative Medicine/Additive Manufacturing in Biomedical Research and Active Packing Materials

Guzzinati Giulio	#212	Metamaterials, Plasmonics and Nanophotonic systems
Hirata Ikue	#176	Organic/Hybrid and Printed Electronics and Photonics
Jugovac Matteo	#123	Growth and Synthesis of 2D Materials
Kopula Kesavan Jagadesh	#108	Materials and Processing for Energy
Kovtun Alessandro	#207	Fundamental Physical Properties of 2D Materials and their Heterostructures
kumar Abhishek	#096	Molecular self-assembly and self-organized nano and mesostructures
La Deda Massimo	#008	Colloidal particles and nanoparticles
La Rosa Marcello	#017	Metamaterials, Plasmonics and Nanophotonic systems
Lamperti Alessio	#164	Advanced Structural Characterization of 2D Materials
Leporatti Stefano	#184	Nanobiocomposites for In-vitro Diagnostics and Targeted Drugs
Leuzzi Luca	#041	Photophysical and Non-linear Phenomena
Liscio Fabiola	#011	Colloidal particles and nanoparticles
Lizzit Daniel	#121	Growth and Synthesis of 2D Materials
Lo Porto Chiara	#180	Nanobiocomposites for In-vitro Diagnostics and Targeted Drugs
Longo Massimo	#220	Advanced Nanofabrication and Characterization of Electronic and Photonic Devices
Lorenzoni Andrea	#203	Organic/Hybrid and Printed Electronics and Photonics
Luches Paola	#006	Materials and Modelling for Energy Conversion
Lunedei Eugenio	#037	Photophysical and Non-linear Phenomena
Magnozzi Michele	#166	Advanced Structural Characterization of 2D Materials
Magnozzi Michele	#216	Metamaterials, Plasmonics and Nanophotonic systems
Marini Diego	#040	Photophysical and Non-linear Phenomena
Martella Christian	#210	Fundamental Physical Properties of 2D Materials and their Heterostructures
Mastria Rosanna	#170	Chemical Functionalization and Characterization of 2D Materials
Matteocci Fabio	#075	Materials and Processing for Energy
Mazzaglia Antonino	#181	Nanobiocomposites for In-vitro Diagnostics and Targeted Drugs
Melloni Filippo	#238	Organic/Hybrid and Printed Electronics and Photonics
Merano Michele	#236	First Principles Modelling of 2D Materials and their Heterostructures
Milano Gianluca	#246	Low-dimensional Structures for Nanoelectronics and Nanophotonics
Milita Silvia	#050	Materials and Modelling for Energy Conversion
Miskovic Vanja	#240	Organic/Hybrid and Printed Electronics and Photonics
Missori Mauro	#024	Cultural Heritage
Molteni Elena	#044	Computational and experimental methods for soft matter
Monforte Francesca	#259	Materials and Technologies for Energy Storage
Montesi Monica	#183	Nanobiocomposites for In-vitro Diagnostics and Targeted Drugs
Morandi Vittorio	#098	2D Materials for Energy and Environmental Applications
Moschetto Salvatore	#169	Chemical Functionalization and Characterization of 2D Materials
Mossa Stefano	#033	Materials and Modelling for Energy Conversion
Munaò Gianmarco	#013	Colloidal particles and nanoparticles
Nardi Martina	#135	Stimuli-responsive materials
Natali Marco	#083	Biomaterials for Regenerative Medicine

Natali Murri Annalisa	#109	Materials and Processes for Environment Protection and Sustainability
Nava Diego	#202	Organic/Hybrid and Printed Electronics and Photonics
Ngoc Tran Lam Thi	#140	Low-dimensional Structures for Nanoelectronics and Nanophotonics
Nobili Francesco	#258	Materials and Technologies for Energy Storage
Orbelli Biroli Alessio	#051	Materials and Modelling for Energy Conversion
Orsi Davide	#090	Molecular self-assembly and self-organized nano and mesostructures
Ortolani Luca	#120	Growth and Synthesis of 2D Materials
Pagliusi Pasquale	#068	Molecular self-assembly and supramolecular materials
Pagliusi Pasquale	#038	Photophysical and Non-linear Phenomena
Palma Amedeo	#030	Materials and Modelling for Energy Conversion
Palummo Maurizia	#232	First Principles Modelling of 2D Materials and their Heterostructures
Panighel Mirco	#209	Fundamental Physical Properties of 2D Materials and their Heterostructures
Panseri Silvia	#084	Biomaterials for Regenerative Medicine
Pasini Mariacecilia	#174	Organic/Hybrid and Printed Electronics and Photonics
Pasquini Luca	#078	Materials and Processing for Energy
Passaglia Elisa	#129	Organic, polymer and hybrid nanostructures, and bio soft materials
Pastoriza-Santos isabel	#214	Metamaterials, Plasmonics and Nanophotonic systems
Patrizi Barbara	#039	Photophysical and Non-linear Phenomena
Peddis Davide	#178	Organic/Hybrid and Printed Electronics and Photonics
Pellegrino Francesco	#114	Materials and Processes for Environment Protection and Sustainability
Pelli Cresi Jacopo Stefano	#004	Materials and Modelling for Energy Conversion
Perinot Andrea	#241	Organic/Hybrid and Printed Electronics and Photonics
Pica Monica	#171	Chemical Functionalization and Characterization of 2D Materials
Piccirillo Clara	#059	Materials and Processes for Environment Protection and Sustainability
Pierleoni Davide	#208	Fundamental Physical Properties of 2D Materials and their Heterostructures
Pietralunga Silvia Maria	#143	Low-dimensional Structures for Nanoelectronics and Nanophotonics
Pisignano Dario	#127	Organic, polymer and hybrid nanostructures, and bio soft materials
Pontiroli Daniele	#097	2D Materials for Energy and Environmental Applications
Prete Domenic	#247	Low-dimensional Structures for Nanoelectronics and Nanophotonics
Preti Lorenzo	#085	Biomaterials for Regenerative Medicine
Previtali Barbara	#219	Advanced Nanofabrication and Characterization of Electronic and Photonic Devices
Prosa Mario	#200	Organic/Hybrid and Printed Electronics and Photonics
Pugliese Marco	#058	Materials and Processes for Environment Protection and Sustainability
Racine Benoit	#199	Organic/Hybrid and Printed Electronics and Photonics
Ravoo Bart Jan	#133	Stimuli-responsive materials
Reale Andrea	#003	Materials and Modelling for Energy Conversion
Restuccia Paolo	#100	2D Materials for Energy and Environmental Applications
Ricciardi Loredana	#009	Colloidal particles and nanoparticles
Riccò Mauro	#255	Materials and Technologies for Energy Storage
Righetti Maria Cristina	#131	Organic, polymer and hybrid nanostructures, and bio soft materials

Righi Giulia	#257	Materials and Technologies for Energy Storage
Righi Maria Clelia	#031	Materials and Modelling for Energy Conversion
Rigoni Carlo	#139	Stimuli-responsive materials
Ritacco Tiziana	#223	Advanced Nanofabrication and Characterization of Electronic and Photonic Devices
Roccaforte Fabrizio	#197	Advanced Nanofabrication and Characterization of Electronic and Photonic Devices
Romano Lucia	#194	Advanced Nanofabrication and Characterization of Electronic and Photonic Devices
Ronetti Flavio	#190	Topology and Electronic Correlation in Magnetism and Superconductivity
Rontani Massimo	#144	Low-dimensional Structures for Nanoelectronics and Nanophotonics
Ruocco Alessandro	#014	Metamaterials, Plasmonics and Nanophotonic systems
Sanchez Ramirez Diego	#113	Materials and Processes for Environment Protection and Sustainability
Sandri Monica	#086	Biomaterials for Regenerative Medicine
Sangiorgi Nicola	#080	Materials and Processing for Energy
Sangiovanni Giorgio	#188	Topology and Electronic Correlation in Magnetism and Superconductivity
Sanna Samuele	#261	Materials and Technologies for Energy Storage
Santoro Mario	#154	Chemical Functionalization and Characterization of 2D Materials
Saracino Emanuela	#116	Biomaterials for Regenerative Medicine/Additive Manufacturing in Biomedical Research and Active Packing Materials
Sartori Paolo	#007	Colloidal particles and nanoparticles
Savio Letizia	#091	Molecular self-assembly and self-organized nano and mesostructures
Scaccabarozzi Alberto	#071	Organic/Hybrid and Printed Electronics and Photonics
Scaravonati Silvio	#260	Materials and Technologies for Energy Storage
Scelta Demetrio	#152	Chemical Functionalization and Characterization of 2D Materials
Schiesaro Irene	#193	Topology and Electronic Correlation in Magnetism and Superconductivity
Scidà Alessandra	#102	2D Materials for Energy and Environmental Applications
Scidà Alessandra	#165	Advanced Structural Characterization of 2D Materials
Scotognella Francesco	#148	Chemical Functionalization and Characterization of 2D Materials
Scotognella Francesco	#149	Chemical Functionalization and Characterization of 2D Materials
Sementa Luca	#029	Materials and Modelling for Energy Conversion
Sensi Matteo	#204	Organic/Hybrid and Printed Electronics and Photonics
Shaidu Yusuf	#107	Materials and Processing for Energy
Silvestrelli Pier Luigi	#043	Computational and experimental methods for soft matter
Smerieri Marco	#126	Growth and Synthesis of 2D Materials
Sorrentino Roberto	#242	Organic/Hybrid and Printed Electronics and Photonics
Sortino Salvatore	#128	Organic, polymer and hybrid nanostructures, and bio soft materials
Sozzani Piero	#061	Molecular self-assembly and supramolecular materials
Stucchi Elena	#239	Organic/Hybrid and Printed Electronics and Photonics
Stupar Matija	#094	Molecular self-assembly and self-organized nano and mesostructures

Tampieri Anna	#082	Biomaterials for Regenerative Medicine
Tessarolo Marta	#230	Electronic and Photonic Devices for Biological Applications
Tessarolo Marta	#118	Biomaterials for Regenerative Medicine/Additive Manufacturing in Biomedical Research and Active Packing Materials
Tino Angela	#132	Organic, polymer and hybrid nanostructures, and bio soft materials
Toci Guido	#036	Photophysical and Non-linear Phenomena
tonazzini ilaria	#186	Nanobiocomposites for In-vitro Diagnostics and Targeted Drugs
Tortiglione Claudia	#182	Nanobiocomposites for In-vitro Diagnostics and Targeted Drugs
Trincini Omar	#221	Advanced Nanofabrication and Characterization of Electronic and Photonic Devices
Trioni Mario Italo	#191	Topology and Electronic Correlation in Magnetism and Superconductivity
Truffa Giachet Francesca	#157	Stimuli Responsive Bioorganic Materials and Smart Surfaces
Ugolotti Aldo	#233	First Principles Modelling of 2D Materials and their Heterostructures
Urso Mario	#106	Materials and Processing for Energy
Ussia Martina	#130	Organic, polymer and hybrid nanostructures, and bio soft materials
Usta Hakan	#173	Organic/Hybrid and Printed Electronics and Photonics
Valt Matteo	#153	Chemical Functionalization and Characterization of 2D Materials
Varvaro Gaspare	#251	Advanced Spintronics and Nanomagnetism: Materials and Devices
Verdini Alberto	#095	Molecular self-assembly and self-organized nano and mesostructures
Veronesi Stefano	#168	Chemical Functionalization and Characterization of 2D Materials
Villa Elena	#002	Materials and Modelling for Energy Conversion
Vinci Antonio	#056	Materials and Processes for Environment Protection and Sustainability
Vurro Vito	#158	Stimuli Responsive Bioorganic Materials and Smart Surfaces
Wolf Heiko	#089	Molecular self-assembly and self-organized nano and mesostructures
Zanfrognini Matteo	#016	Metamaterials, Plasmonics and Nanophotonic systems
Zanotto Simone	#018	Metamaterials, Plasmonics and Nanophotonic systems
Zappia Stefania	#049	Materials and Modelling for Energy Conversion
Zoli Luca	#055	Materials and Processes for Environment Protection and Sustainability
Zontone Federico	#076	Materials and Processing for Energy
Zuccatti Elisabetta	#179	Organic/Hybrid and Printed Electronics and Photonics
