

ACTIVITY REPORT 2018





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Foreword



his is the fourth biennial report of the Institute Nanoscience of the Italian National Research Council (Cnr Nano). In 2016, the scientific activities of Institute Nanoscience were reorganized in five main strategic areas: solid-state quantum technology, fundamental and translational nanobiophysics, nanoscale theory modelling and computation, physics and technology of light at the nanoscale, and surfaces and interfaces: nanofabrication, imaging, and spectroscopy. The highlights of the 2018 Activity Report have been divided into the above mentioned strategic areas.

The main achievement of the Institute Nanoscience in the years 2016 and 2017 is the large number of granted highly competitive projects. In particular, in the framework of the Horizon 2020 program, several new projects have been funded, such as two FET-Open, one ITN, a E-INFRA Centre of Excellence (coordinated by Cnr Nano), and a Quantera project. Another strategic element of the activities of Cnr Nano is the participation in the third phase of the "Graphene" Flagship starting from April 1st, 2018. The Institute of Nanoscience has coordinated for Cnr the NANO4BRAIN project (Cnr "Premiali" projects 2015). A scientific agreement with Microsoft has been established in the framework of synthesis of structures by the selective area growth method. Furthermore, in 2016, an internal call for SEED projects for young researchers has been promoted, and four SEED projects have been granted. The results will be presented during the next scientific meeting of the Institute to be held in 2018.

The large impact of Cnr Nano in the national and international context is demonstrated by the large number of publications in high impact factor journals. In the following pages, information on published papers, funded projects, and the events in the period of 2016-2017 is given.

In the last two years, four permanent researchers and one administrative staff have joined Cnr Nano. Furthermore, a large number of young researchers could join the Institute to work on these national and international projects. Prominent in Cnr Nano is in fact the presence of many fixed-term scientists and post-docs. At present the Institute has 71 staff members and about 28 post-doctoral fellowships, in addition to associated scientists and PhD students.

I would like to thank Luisa Neri, Maddalena Scandola, Giorgia Brancolini, Andrea Camposeo, Stefan Heun, Paola Luches, and Gian Michele Ratto for their help in making this Report.

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Director of Cnr Institute Nanoscience



Highlights -Fundamental and translational nanobiophysics

Introduction to Fundamental and translational nanobiophysics

In these highlights we discuss some active research programs that are well representative of the wide scope of the theoretical and experimental biophysics being performed in the Institute. These activities range from the characterization of the interaction between biological moieties and nanostructured materials all the way to studies on the biophysical substrate of brain disease performed on animal models.

Interactions between nanostructured materials and bio-matter. These projects study the dynamic interfacing of biological entities with nanostructured materials, either by modelling techniques based on prime principles or by *in vitro* analysis of the interaction between cells and patterned bio-materials. A computational approach has been employed to demonstrate that gold nanoparticles can inhibit the dimerization of monomeric elements of the macroglobulin complex. The interactions between biomaterials and soft matter are addressed by an experimental study that developed a novel procedure for the generation of complex nano-configuration of the surface of a biocompatible substrate. This nano-structuring was shown to cause specific effects on the phenotype of glial cells of the peripheral nervous system. The target of these studies is the preparation of scaffolds that might promote the regeneration of peripheral nervoes in vivo.

Bio-photonics: exploring cells with light. These studies share the common theme of harnessing fluorescent molecules as nanoprobes of the intracellular environment. Here it is demonstrated a novel method that uses the statistics of the diffusive process to fingerprint different elements of the intracellular space.

Clustering analysis in a 3-D phase space allowed the automatic segregation of intracellular vescicles without the need of reconstructing the individual trajectories. Fluorescent probes can be analyzed in vitro and in vivo and can be tailored to study the nanoscopic environment surrounding the fluorescent moiety. Two different studies demonstrate the operation of sensors for viscosity, polarity chloride and pH. Some sensors are prone to be employed in vivo in the intact organ, as exemplified by a set of studies on the mechanisms at the basis of several brain diseases. A set of techniques has been developed to study the dysregulation of the neuronal negative feedback that presides at the control of gain in the cortex and that is associated to severe brain diseases such as epilepsy and autism. In particular, a method was demonstrated that contributes to a very long standing open question in neuroscience, which is the quantitative visualization of inhibition in the intact brain.

Theranostic. Other studies are not represented in this sample, but they are worth mentioning since they open new lines of investigation that promise to bring about fallout in the field of theranostic. A line of research is contributing to the development of ingestible light sources that will target the infective agent *Helicobacter pylori* by exploiting the presence of an endogenous pigment that can be targeted with light to induce a photo-damage of the bacteria. On the diagnostic side, a large collaborative project involving groups in the Cnr Nanoscience and Neuroscience Institutes is directed at the identification of molecular marker of brain tumor by means of advanced molecular sensing techniques.

Activity Report 2018

Fingerprinting sub-cellular nanostructures by spatiotemporal fluctuation spectroscopy and single particle tracking

We demonstrated that image mean square displacement (iMSD) analysis is a fast and robust platform to address living matter structural and dynamic organization at the level of sub-cellular nanostructures, with no a-priori knowledge of the system, and no need to extract single trajectories. From each iMSD we extracted a unique triplet of average parameters (diffusivity, anomalous coefficient, size) and we plotted them in a 3D parametric space, where clustering of single-cell points readily defines the structure "dynamic fingerprint" at the whole-cell-population level. We demonstrated that different sub-cellular structures segregate into separate regions of the parametric space. The potency of this approach is proved through application to exemplary biological cases.

Sub-cellular sub-micrometric and dynamic organelles or compartments determine how cells are able to comply with internal or external stimuli in both physiological and pathological conditions. In spite of their importance, observing subcellular structures at high spatial and temporal resolution in living cells is a challenging task. We recently proposed a fluorescence-based spatiotemporal fluctuation analysis method able to extract quantitative information on diffusing objects directly from imaging, in the form of a mean square displacement (MSD) vs time-delay plot (hereafter iMSD) [1,2] (Fig. 1A-C). The iMSD approach does neither need preliminary as-



Fig. 1

Schematic representation of the *i*MSD-based dynamic fingerprint analysis. A) A stack of images of fluorescently-labelled intracellular structures is acquired by time-lapse confocal microscopy. B) Spatiotemporal correlation function is derived from image analysis by the *i*MSD algorithm. C) Gaussian fitting of correlation functions allows to extract the *i*MSD plot, which in turn depicts the average diffusion law of the structure of interest (exemplary cases are reported: super-diffusion, dotted red line; isotropic diffusion, dashed red line; sub-diffusion, solid red line). D) Three relevant parameters are chosen from the fitting equation to quantitatively describe the average dynamic properties of the structures of interest, namely: the short-range diffusion coefficient (D_m), the anomalous diffusion coefficient (a), and the *y*-axis intercept of the *i*MSD plot, indicating the average apparent size of the diffusing structures. These three parameters are organized in a 3D plot, used to identify the 'dynamic fingerprint' of the diffusing structure.

sumptions on the system nor to extract trajectories. Importantly, the iMSD plot simultaneously yields structural (size and morphology) and dynamical (diffusivity and type of motion) information.

From each iMSD, a triplet of average parameters (i.e., diffusivity, anomalous coefficient, size) are extracted and represented in a 3D parametric space, where clustering of single-cell points readily defines the structure "fingerprint" (Fig. 1D). The potency of this approach was proved in some exemplary biological cases. First, we demonstrated that the classical sub-cellular structures involved in the endocytosis process (e.g., caveolae, clathrin-coated pits, macropinosomes) are characterized by well-distinguished structural and dynamic fingerprints [3] (Fig. 2). Then, focusing on macropinosomes, we were able to monitor for the first time its evolving dynamic and structural nature [3] (Fig. 3), which was so far postulated only on the basis of biochemical assays. Based on this knowledge, we used iMSD to demonstrate that a biomolecular corona adsorbed on lipid nanoparticles promotes a neat switch of their cell-entry mechanism and intracellular trafficking, from macropinocytosis to clathrin-dependent endocytosis [4]. Finally, exploiting existing collaborations at NEST laboratory, we are currently applying the iMSD approach to analyze lysosome finger-print in cellular models of Krabbe disease.

As a perspective, we plan to combine the *i*MSD approach to Single Particle Tracking (SPT) analysis (already exploited at NEST for studying neurotrophin receptors and their ligands [5,6]), in order to analyze the dynamic fingerprint at the level of trajectories and to highlight heterogeneities and correlated dispersions of the structural and dynamic properties of the structures of interest.

Fig. 2

Dynamic fingerprint of exemplary intracellular nanostructures. A) Representative confocal images clathrin-coated of vesicles, macropinosomes, and caveolae, respectively (green signals). The blue signal indicates the nucleus. Scale bar: 10 µm. B) Represenplots of the tative three structures (cla-



thrin-coated vesicles in blue, macropinosomes in green, and caveolae in red). C) 3D plot of extracted parameters shows the differences in the dynamic (short-range diffusivity and anomalous coefficient) and structural (size) properties of the selected structures.



Fig. 3

The time evolution of the macropinosome dynamic fingerprint. A) Exemplary *i*MSD plots of macropinosomes at three different stages of trafficking: early (30-70 min), intermediate (80-120 min), and late (>130 min). B) 3D plot showing the time evolution of the dynamic fingerprint of macropinosomes from early (light green) to intermediate (white) and finally late (dark green) stages of trafficking.

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Hierarchical thermoplastic rippled nanostructures regulate Schwann cell adhesion, morphology and spatial organization

Here, anisotropic hierarchical rippled nanotopographies with a lateral periodicity of ~300 nm are produced from a gold-irradiated germanium mold in polyethylene terephthalate, a biocompatible polymer approved by the US Food and Drug Administration for clinical applications, by a novel three-step embossing process. The effects of nano-ripples on Schwann Cells (SCs) are studied in view of their possible use for nerve-repair applications. The data demonstrate that nano-ripples can enhance short-term SC adhesion and proliferation, drive their actin cytoskeleton spatial organization and sustain long-term cell growth. Notably, SCs are oriented perpendicularly with respect to the nanopattern lines.

Here, we have studied the effects of new multiscale periodic structures on SC behavior by pure contact interaction in view of the possible use for nerve-repair applications. The periodic rippled nanotopographies are a recently introduced type of hierarchical and anisotropic nanostructures that can be obtained when the surface of germanium (Ge) is irradiated with gold ions incident at an oblique angle. These Ge substrates were replicated by an innovative three-step fabrication process onto polyethylene terephthalate (PET) surfaces (Fig. 1). Two kinds of PET substrates were generated, named Ripple Low-Dose (RLD) and Ripple High-Dose (RHD), with a typical spatial period of 270 \pm 40 nm (RLD) and 290 \pm 30 nm (RHD), and increased hydrophobicity and roughness.

SCs were cultured on these substrates for one week, analyzed by microscopy and assayed for adhesion, spreading and proliferation (Fig. 2). These experiments demonstrated that PET nano-ripples are suitable for SCs, determining an increased short-term cell adhesion (3 h) and viability (24 h), in particular on RHD; at longer term (48 and 96 h and 1 week), the proliferation rate and viability were comparable to those of the control flat conditions. Moreover, SCs actively interacted with nano-rippled topographies, and polarized in a perpendicular direction with respect to the pattern lines (Fig. 3).

By actin fiber staining and quantitative confocal fluorescence microscopy we confirmed that the high degree of perpendicular SC polarization also holds for the actin cytoskeleton. Data also suggested that on these substrates the actin content can be increased in cells with perpendicular alignment with respect to those with parallel alignment. Since topographical modification of the cell/substrate interface is an important regulator of cellular adhesion and function, our results provide information on the possible use of hierarchical nanometric elements for tissue engineering applications.



Fig. 2

(a) Bright field images of Schwann cells cultured on flat, RLD and RHD periodic nano-rippled PET replicas 3 h, 24 h, and 48 h after seeding. Scale bar: 50 µm. Arrows indicate the nano-ripple direction. (b) Percentage of spread cells at 3 h. (c–e) SC cell viability 24 h, 48 h and 96 h after seeding. Data are the mean \pm SEM, $n \ge 3$; * P < 0.05, one-way ANOVA, Dunnett's test vs. flat. (f) Representative confocal images of SCs cultured for 7 days on flat, RLD, and RHD, and immuno-stained for S100 (green), actin (red) and nuclei (blue). SCs proliferated and reached confluence on nanoripples and flat surfaces. Scale bar: 50 µm; white arrows: ripple direction.

Fig. 1

Schematic description of the fabrication process and the corresponding atomic force microscopy images. (a) PFPE intermediate molds obtained by a UV-crosslinking process for both RLD and RHD periodic nano-rippled features; (b) thermal nanoimprint lithography process with PFPE intermediate molds to obtain COC replicas; (c) PET nano-rippled replicas obtained by thermal NIL. Scale bar: 1 µm.





Fig. 3

(a) Confocal microscopy images of Schwann cells on flat, RLD and RHD nano-rippled PET stained for S100 (green) and nuclei (blue). Scale bar: 100 μ m. Arrows indicate the nano-ripple direction. (b–c) SC morphological characterization: cell area (b) and aspect ratio (c) for the different substrates. (d) Cell angular distribution (0° is the nano-ripple direction) for the different patterns. Data are the mean ± SEM, n = 3; (c): **P < 0.01, one-way ANOVA, Dunnett's test vs. flat.

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Proper brain computation requires a fine equilibrium between a positive neuronal feed-back, necessary to recruit large neuronal ensembles responsible for computation and behavioral responses to the ever changing environment, and a negative feedback that maintains activity within the rather limited dynamic range available to neurons. The inhibitory feedback is provided by the activity of a specific set of inhibitory synapses permeable to chloride. The direction of chloride flux determines the extent of neuronal inhibition and these currents depend critically on the intracellular concentration of chloride. In a set of four studies we have achieved methodological and basic science advancements in this important field.

The excitation/inhibition equilibrium is a dynamic process in continuous evolution during daily activity and during sleep. The key effector of inhibition is a class of inhibitory neurons that uses gamma amino butyric acid (GABA) as a neurotransmitter. When GABA is released at the synapse a chloride channel opens and, if intracellular chloride is low enough, the entrance of negative charges renders the neuron more negative thus opposing the effects of excitation (Fig. 1A). A correct operation of this feedback is absolutely essential for proper brain computation as demonstrated by the fact that, disruptions of this system leads unavoidably to some form of brain pathology. In the first study we discuss [2], we disrupted the inhibitory feedback by treating a patch of the mouse brain with a drug that reduces the efficacy of the inhibitory synapses. The immediate consequence of this treatment is the onset of epileptic activity in the treated cortical domain as shown by the very large periodic peaks in the extracellular potential (interictal spikes, IS). By means of simultaneous patch clamp we have shown that these events are associated to short synchronous bursts of action potentials (Fig. 1B). Computation is obviously abolished in this circuitry, but we wondered whether these transient large events could interfere with cortical computation in nearby connected areas. Indeed, we determined that even if ISs did not invade the opposite hemisphere, the EEG was subtly disrupted. By phase-locked averaging of the LFP we found that every IS caused a peculiar change of the firing probability of the contralateral hemisphere: initially the ISs facilitated firing in this area but, after about 100 ms, the cortex was completely silenced for almost 300 ms. Finally, we determined that visual evoked responses were affected by ISs depending on the temporal relationship between stimulus presentation and contralateral spike burst (Fig. 1C).

Given that inhibitory currents are mostly carried by chloride, its intracellular concentration ($[Cl]_i$) dictates the direction of these currents and the result of their action: low $[Cl]_i$ leading to inhibition and high $[Cl]_i$ leading to depolarisation. The regulation of $[Cl]_i$ exerts wide-ranging effects on synaptic signaling and plasticity and on development and disorders of the brain. In the last few years we developed a technique for the measurement of $[Cl-]_i$ by means of two-photon imaging and spectroscopy. In this study we had to develop specific hardware for the control of the spectroscopic measurements [3] and for the delivery of the genetic sensor [4]. Our genetically encoded fluorescent sensor includes a spectroscopic reference (Fig. 2) and we were able to perform parallel measurements of $[Cl]_i$ and pH at the single-cell level in the mouse cortex in vivo [1].



Fig. 1

A) Schematic representation of the interaction between inhibitory and excitatory neurons. Gain adaptation is one of the fundamental computations performed by cortical micro-circuitry. Weak synaptic inputs, such as those evoked by a low-contrast visual stimulus, must be amplified substantially in order to produce a detectable response. As the synaptic input increases, amplification must be reduced to avoid response saturation (dotted green lines on the right panels). Several mechanisms participate in this non-linear computation, with an especially important role played by the reciprocal equilibrium between inhibitory interneurons and pyramidal neurons. As synaptic input increases, interneurons are recruited at an increasing rate and their feedback on pyramidal cells shift the response function to the right (continuous green lines). B) Loose-patch recording from a L2/3 neuron during interictal activity (upper trace) and the simultaneous LFP recording from a nearby extracellular electrode. The inset shows the neuronal firing during a single IS event. C) Mean VEP waveforms recorded in the same mouse at three different contrasts for different relative timing between the stimulus presentation and the interictal spike.



Fig. 2

A) The chloride/pH sensor is formed by the fusion of the CI sensitive element E²GFP with the insensitive spectral reference LSSmKate2. E²GFP is sensitive to both intracellular pH and [CI], Changes in pH are reported with a shift of the 2-photon excitation spectra. Chloride interacts with the chromophore by collisional quenching, therefore increasing [CI], is reported as a decrement of the green fluorescence in comparison with the red reference. The plot shows the two-photon excitation spectra of E²GFP and LSSmKate2 at different levels of pH. The non-labeled spectra of E²GFP have been obtained at pH 6.4, 6.8, 6.9, 7.1, 7.2, 7.4, and 7.6. The excitation spectrum of LSSmKate2 is pH-insensitive: the lower panel shows the normalized difference between the spectra obtained at pH values of 6, 7, and 8, with the mean spectrum averaged for all pHs. B) Expression and spectra of LSSmClopHensor in vivo after transfection by in utero electroporation. The field depicted lies in the superficial layers of the visual cortex. Calibration bar 100 μ m. C) Measurement of intracellular Chloride in the mouse cortex: it is clear that different cells display different hues from green to orange, with low chloride cells appearing green. Numbers in the lower panel report the computed concentrations.

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New fluorescent biosensors for functional imaging of cells and diagnostic applications at the nanoscale

Fluorescence offers the unique opportunity to combine high detection sensitivity (down to single molecule detection) and spatial imaging resolution, with an optical signal responsive to nanoscale changes of environmental physicochemical properties. Here, we shall show how the rational design of the chemical structure transforms organic dyes into efficient biosensors of dielectric and viscosity properties with confocal spatial resolution (200 nm) at intracellular level. These environmental biosensors were effectively applied to image physicochemical properties of intracellular organelles, shedding light on several biomedically-relevant phenomena including drug delivery mechanisms and chromatin compaction upon nuclear lamina misassembly in the Hutchinson-Guilford progeria syndrome.

Intracellular polarity and viscosity play regulative roles irrespective of the specific nature of any biochemical reaction. Accordingly, intensive research has been recently devoted to polarity/viscosity fluorescent sensors for high-resolution fluorescent microscopy. Usually, polarity affects the energy of emission, whereas viscosity effectively modulates the fluorescent lifetime.

By a combined computational and experimental approach, we developed fluorescent "molecular rotors" able to monitor independently intracellular polarity and viscosity [1]. These probes provided quantitative measurements of polarity and viscosity of the endosomal membrane. Real time monitoring of polarity and viscosity allowed for

Fig. 1

Left panel: molecular structure of the dual (dielectric polarity constant, ε) / viscosity (n) fluorescent sensor Gel conjugated to the membrane-active peptides Tat, and/or CM₁₈. Right panel: administration of conjugated Gel to Hamster Ovary Cells cells. (a) Transmission. Fluorescence, $Log(\varepsilon)$ and $Log(\eta)$ maps of cells treated with CM₁₀-Gel



Transmissio

Fluoresco

(upper panels), CM_{18} -Tat₁₁-Ge1 (medium panels) and Tat₁₁-Ge1 (lower panels). (b) Zoomed region (white squares in panel a) of CM_{18} -Tat₁₁-Ge1 treated cells. Polarity and viscosity data clearly show that mono-substituted Tat₁₁-Ge1 and CM_{18} -Ge1 remain entrapped inside the endosomal membranes; conversely, the fusion construct CM_{18} -Tat₁₁-Ge1 disrupt the lipid bilayer, as witnessed by the much lower viscosity and higher polarity, and allows for cargo release to the cytoplasm.

Log(s) map

Log(n) mag

validating engineered drug delivery peptides able to disrupt the lipid bilayer once internalized, thus providing a novel assay of drug delivery efficacy (Fig. 1).

As an alternative approach, we focused on a peculiar fluorescent "molecular rotor", whose excited state is unaffected by local polarity [2]. According to a strategy previously established by us [Battisti 2013], we followed the lifetime-viscosity dependence by the phasor approach to fluorescence lifetime imaging, a fit-free graphical method based on the frequency-domain analysis of the fluorescence decay. Our probe highlighted that cells characterized by a genetically-encoded misassembly of lamin A, as observed in Hutchinson-Gilford progeria syndrome (HGPS) [2], are associated with a reduced nucleoplasm viscosity (Fig. 2), supporting a strict correlation between HGPS and chromatin compaction and regulation.

Complementary to these approaches, a coumarine derivative was demonstrated to possess two concomitantly emitting excited states with different energies, breaking the so-called Kasha's rule [Brancato 2015]. On account of its unique photophysics, this probe was applied to cell imaging to report both the dielectric constant and the water content of subcellular regions.

In conclusion, on account of the exquisite sensitivity of fluorescence, we developed a toolbox of intracellular sensors to monitor polarity and viscosity of nano-environments, in view of diagnostic applications.

Fig. 2

Left panel: molecular structure of the polarity-independent viscosity-dependent fluorescent sensor BoMe. Middle panels: BoMe was administered to both health and HGPS-affected human osteosarcoma cells 2 (U2OS), which displayed different structure of



nuclear lamina (round and smooth: healthy cells; irregular and blebbed: HGPS cells). BoMe binds to chromatin and reports on the local viscosity. Right panel: phasor plot of frequency-domain lifetime response of BoMe: different positions on the phasor plot indicate different viscosity values, and are color codified according to cell images in the middle panel. Color distribution clearly shows lower chromatin viscosity for HGPS cells.

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Inhibition of Protein Dimerization with Gold Nanoparticles: D76N and Δ N6 β 2-microglobulin Variants

The relevance of nanoparticle-protein interaction is acquiring increasing relevance crucial in several application contexts. In this study, we present a comprehensive investigation of the interaction between two highly amyloidogenic, naturally occurring variants of β 2-microglobulin, D76N and Δ N6, and gold nanoparticles stabilized by a shell of citrate surfactants (citrate-capped gold nanoparticles) by including novel computational and experimental data. State-of-the-art computational methods (enhanced sampling classical atomistic molecular dynamics and rigid-body protein-surface docking) synergistically combined to experimental data (NMR, thioflavin T fluorescence, native agarose gel electrophoresis and transmission electron microscopy) indicate that AuNPs are able to hamper D76N and Δ N6 β 2m fibrillogenesis through an effective interaction that competes with protofibril formation or recruitment. Results may provide new routes to rescue protein fibrillation or revert their amyloid deposition, and they are relevant to any application which depends on the physico-chemical characteristics of the nanoparticles.

Experiments have shown that inorganic nanoparticles stabilized by a shell of organic surfactants can enhance or suppress the natural propensity of proteins to form fibrils, depending on the protein and the nanoparticles. In particular citrate-coated gold nanoparticles (cit-AuNPs) were recently investigated with amyloidogenic protein β 2-microglobulin (β 2m) [1], protein aggregation including the formation of dimers and multimers in solution, underlies an array of human diseases such as systemic amyloidosis which is a fatal disease caused by misfolding of native globular proteins damaging the structure and function of affected organs.

We present a comparison between atomistic simulations and NMR experiments, on two challenging models known for their enhanced amyloidogenic propensity, namely $\Delta N6$ and D76N $\beta 2m$ naturally occurring variants, and disclose the role of cit-AuNPs on their fibrillogenesis [2]. The proposed interaction mechanism lies in the interference of the cit-AuNPs with the protein dimers at the early stages of aggregation that induces dimer disassembling. As a consequence, natural fibril formation can be inhibited.

Contrary to previous results reported in the literature and obtained with other nanoparticles such as polymeric nanoparticles, cerium oxide nanoparticles, quantum dots and carbon nanotubes, that were found to promote $\beta 2m$ fibrillogenesis, cit-AuNPs was able to hamper D76N and $\Delta N6 \beta 2m$ fibril deposition. These data suggest the opening of new perspectives for the treatment with nanoparticle of amyloidogenic proteins.



Fig. 1

Computational and NMR results. Left Panel: Most stable orientations of the D76N dimers interacting with cit-AuNP. Direct contacts of the sub-unit 1 (green) and sub-unit 2 (cyan) are highlighted with balls on the α Carbon atoms. Right Panel: a) Overlay of 15N-1H HSQC spectra of 15N-labelled D76N β 2m (18 μ M) in the free form in blue and in the presence of 90 nM cit-AuNP. b) Bar plot of relative intensity calculated from the comparison between the spectra reported in a). c) D76N β 2m cartoon highlighting the residue locations that proved most affected by cit-AuNPs, i.e., displaced one standard deviation at least with respect to the average relative intensity.

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Highlights -Physics and technology of light at the nanoscale

Introduction to Physics and technology of light at the nanoscale

The research activities in the thematic area of "Physics and technologies of light at the nanoscale" are aimed at understanding the properties of light confined to nanoscale volumes and interacting with nanostructured materials. These include the synthesis and growth of organic and inorganic nanomaterials (nanowires, 2D materials and nanofibers) with tailored optoelectronic properties, the modelling and experimental investigation of the properties of the developed nanostructures, and the design and fabrication of advanced photonic and optoelectronic devices, such as light sources, lasers, photodetectors, microcavities and waveguides. The impact of these technologies ranges across various applications such as optical sensing, high-resolution microscopy, information and communication technologies.

Subwavelength control of light. Semiconducting nanowires constitute powerful building blocks for controlling light at nanoscale, allowing light to be generated and detected with nanoscale spatial resolution, or to be confined to subwavelength volumes by coupling to plasmon resonances of nanowires. Light sources with nanoscale emission spots are fabricated employing hybrid metal-GaAs nanowires, with emission modulated electrically up to 1 GHz. Near-field terahertz (THz) imaging have been demonstrated by using InAs nanowires and black phosphorous flakes as nanodetectors. In addition, semiconducting nanowires can be engineered with a graded doping profile, allowing their plasmon resonance to be spatially-tuned by field-effect carrier modulation. Ultrafast optical switching of plasmon-phonon polaritons has been demonstrated in black phosphorus/SiO, heterostructures. THz micro-resonators and laser sources engineering. Laser sources and detectors in the THz frequency range are being developed, relevant for security and sensing. THz Quantum Cascade Lasers (OCLs) are designed and realized to feature intense, small angle (10°) vertical emission, as well as continuous-wave operation, by means of subwavelength cavities made of two cylindrical, double-metal resonators coupled with a suspended metallic bridge. Other approaches include the fabrication of distributed feedback wire THz OCL and random THz lasers. In view of developing passively mode-locked THz laser source, THz saturable absorbers have been fabricated by transfer coating and inkjet printing of single and few-layers of graphene. In addition, field effect transistors with a few-layer black phosphorus flake are demonstrated to be efficient THz photodetectors for light in the 300 GHz-3.5 THz frequency range, while operating at room temperature.

Photophysics of organic semiconductors. Investigation of photo-excited species in nanostructures made by conjugated polymers and hybrid compounds is currently carried out both experimentally and theoretically, with the aim of tailoring and controlling both radiative recombination processes and light-to-current conversion in flexible nanostructured conjugated polymers and optoelectronic devices. Recently, ultrafast two-dimensional electronic spectroscopy has revealed the dynamics of polaron pairs in a conjugated polymer on a sub-20-fs time scale, and the role of coherent vibronic coupling, which accelerates charge separation dynamics and makes the process insensitive to disorder.

Subwavelength control of light in semiconductor nanowires

The manipulation of light below the diffraction limit attracts much attention owing to its potential impact on sensing, microscopy, and computation and communication technologies. We investigated nanowire-based hybrid electronic/plasmonic systems, possible building-blocks for novel nano-optoelectronic chips embedding multiple functionalities. We engineered individual semiconductor nanowire devices that allowed us to demonstrate a novel technique for the realization of subwavelength light sources operating at 1 GHz. In addition, we proved localization and field-effect control of the plasmon resonance in semiconductor nanostructures with a spatial resolution of 20 nm.

Light sources with nanoscale emission spots are regarded as an alternative tool to aperture-based near-field optical systems for the implementation of microscopy techniques not subjected to the diffraction limit. The coupling between light and collective electron density oscillations (plasmons) is exploited by nanoplasmonics to bypass the stringent limits imposed by diffraction, enabling confinement of light to subwavelength volumes. In this context, starting from individual III-V semiconductor nanowires, we designed and engineered optoelectronic and plasmonic nanodevices with innovative functionalities, based on the unique properties of the nanowires that allow the subwavelength manipulation of light.

On the one hand, we demonstrated a novel technique for the realization of subwavelength light sources operating at 1 GHz [1,2]. We realized hybrid metal-GaAs nanowire devices by controlled thermal annealing of Ni/Au electrodes, and investigated the metallic phases observed in the nanostructure body. Devices were fabricated onto a SiN membrane compatible with transmission electron microscopy studies. Energy dispersive X-ray spectroscopy allowed us to show that the nanowire body includes two Ni-rich phases that, thanks to an innovative use of electron diffraction tomography, were unambiguously identified as Ni₂GaAs and Ni₂As₂ crystals. Using the annealing technique, we prepared hybrid metal-GaAs nanowires embedding two sharp axial Schottky barriers acting as nanoscale point-sources of light. Visible-light electroluminescence was reported upon suitable voltage biasing of the junctions. We investigated the time-resolved emission properties of our devices and demonstrated an electrical modulation of light generation up to 1 GHz. We explored different drive configurations and discussed the intrinsic bottlenecks of the presented device architecture. Our results demonstrated a novel technique for the realization of fast subwavelength light sources, with possible applications in sensing and microscopy beyond the diffraction limit.

On the other hand, we demonstrated localization and field-effect control of the plasmon resonance in semiconductor nanowires with a spatial resolution of 20 nm [3], using scattering-type scanning near-field optical microscopy in the mid-infrared region. To this aim, we adopted InAs nanowires embedding a graded doping profile to modulate the free carrier density along the axial direction. Our near-field measurements had a spatial resolution of 20 nm and demonstrated the presence of a local resonant feature whose position was controlled by a back-gate bias voltage. In our implementation, the field-effect induces a modulation of the free carrier density profile yielding a spatial shift of the plasmon resonance of the order of 100 nm. The relevance of our electrically tunable nanoplasmonic architectures was discussed in view of innovative optoelectronic devices concepts.



Fig. 1

Top panels. Electron diffraction tomography in a single nanowire-based device. N-doped GaAs NWs were deposited onto a SiN membrane and contacted by two Ni/Au (10/100 nm) ~300 nm wide electrodes. The SiN membrane, transparent to electrons, is supported by a thicker silica membrane with a central hole allowing the electrons to pass through the sample, which can be tilted by an angle α around the x-axis. Diffraction patterns were measured at different angles, and merged via dedicated software to obtain a 3D reconstruction of the reciprocal lattice. Bottom panels. Fast light emission in nanoscale point sources. In devices with two Schottky junctions, upon large bias excitation at frequency ω that alternatively drives both the Schottky barriers in the reverse breakdown regime, emitted light is modulated at frequency 2ω .



Fig. 2

We created a linear modulation of the carrier density profile n(x) as a function of the axial position x along an InAs nanowire. The induced density ranges from a nominally undoped value n $\approx 1 \times 10^{16}$ cm⁻³ (in the position labeled by the letter S) to a maximum doping n $\approx 5 \times 10^{18}$ cm⁻³ (in the position labeled by the letter E). An intermediate-doping segment was introduced in the growth sequence and used as marker (M) for the s-SNOM maps. The resulting graded-doping NW is sketched at the bottom of the diagram: the gray color modulation reflects the amount of doping in the NW body (with dark gray meaning high carrier concentration), while the yellow half sphere represents the metallic (Au) tip of the NW. NWs were deposited on a SiO_/Si substrate and contacted by a Ni/Au electrode. The bulk silicon was degenerately n-doped and thus can act as a back-gate upon application of a bias voltage. VG (cross-sectional sketch), provided that a ground reference is set for the NW. A λ = 10.5 µm laser beam (red arrows) is focused on an s-SNOM tip oscillating at 250 kHz. The laser impinging on the tip was vertically polarized with the wave vector forming an angle of 30° with the surface of the NW. The amplitude s and phase ϕ of the reflected beam (blue arrow) are detected using an interferometric pseudoheterodyne technique, demodulated at the fourth harmonic of the tip tapping frequency and used to reveal the local dielectric response of the NW. Phase modulation was achieved as a function of the gate voltage VG. A strong hysteresis was observed by sweeping the gate voltage from low to high values (blue curve) and back (red curve).

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Continuous-wave laser operation of a dipole antenna terahertz microresonator

Resonators rely on different concepts to store and build-up electromagnetic fields in the radio or optical frequencies. In the terahertz range, intriguing possibilities emerge from merging ideas belonging to the electronics and photonics realms. As an application of this feature we realize a quantum cascade laser (QCL) based on whispering gallery mode (WGM) microdisk resonators arranged to compose a dipole antenna. Exploiting the high quality factors of microdisks and the far field control of the antenna element, we obtain a ~3.5 THz laser working in continuous-wave up to 50 K with a narrow vertical emission ($\pm 10^\circ$). The subwavelength device footprint, the low threshold current of 6 mA and a peak power larger than 100 mW make this new kind of device suitable for next generation THz devices for field operations.

Despite the rapid spreading of THz related technology and the existence of sources with high-spectral purity and small footprints such as the QCLs, some limitations prevent the jump from laboratories to real world commercial applications. In particular, the high-confining, routinely used double metal cavities have a subwavelength thickness; while this is not an issue for the plasmonic modes within the waveguide, photons spread laterally due to diffraction when they reach free space through the laser facet. Together with intersubband selection rules which forbid TE-polarized optical transitions, light extraction from a THz QCL has been a long standing issue which still does not have a definite solution, even though brilliant solutions exist.

Our personal approach starts from the modes of a microdisk resonator. Localized at the disk rim, the WGMs can be labeled by counting the nodes of the electric fields along the rim itself. When two disks are placed close to each other, supermodes are formed, with all the possible combinations of even/odd symmetries. By placing an additional suspended bridge between the disks, which is further used to electrically address the device (see Fig. 1(a)), some effects are produced: the modes with even symmetry with respect to \hat{x} mirroring are impaired by the existence of a virtual ground, while the odd ones are mostly unaffected thanks to their field distributions. Moreover, for the mode belonging to the latter family and even with respect to the \hat{y} mirroring, the bridge shapes the field locally as a linear dipole, which makes the far-field converge in a finite lobe in the vertical direction. A finite-element method (FEM) simulation of this mode (which we label $M_{6\rightarrow}$, considering the azimuthal mode family (6) and parity for \hat{x}/\hat{y} mirroring (+/-, respectively)) is shown in Fig. 1 (b), together with the other supermodes.

If the coupling between the disks is properly balanced with the radiative loss, a strong vertical emission is expected, as can be seen for the central simulation in Fig. 1 (c), where the far-field pattern in the $\sqrt{2}$ plane has been extracted using the Stratton-Chu formula. When the disk radius is decreased, the radial loss rate is increased and two lateral lobes appear in the far-field, with a residual lobe in the vertical direction (leftmost simulation in (c)). On the other hand, if the radius is increased, the coupling rate

is reduced and the radial losses are dominating the far-field (rightmost simulation in (c)). Following these considerations, we fabricated an optimized laser (see Fig. 1 (a)). Fig. 2 (a) reports its I-V and L-I (CW) characteristics together with the emission spectrum (inset). The good laser properties are accompanied by a focused emission as can be seen in the far-field pattern of Fig. 2(b), where the simulated far-field is reported as a white-dashed line, showing a good agreement between experiment and simulation.

(c)

R = 14um

Fig. 1

(a) False-color SEM micrograph of the final device. The heterostructure (purple) is sandwiched between two metal layers which can be biased by a DC voltage. (b) Different supermode symmetries originating from the 6-antinodes WGM M_6 in the single disk. The mode relevant for dipole-antenna emission is highlighted by a red square. (c) FEM simulation and far-field pattern in the yz plane for a small radius design (left), where the radiative losses are too strong with respect to the coupling, a large radius design (right), with reduced coupling strength and a balanced design (center) with a dominant vertical emission.



(a) I-V and L-I characteristics of the dipole-antenna THz laser. In the inset the emission spectrum is shown, with a strong dominance of the vertically emitting mode. (b) Measured far-field map. Simulated data is overimposed with dashed white lines.



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F field

R = 24un

(a)

R = 19ur

(b)

M,

THz photonics and nanoelectronics

Recent technological innovation in photonics and nanoelectronics is now enabling Terahertz frequency research to be applied in an increasingly widespread range of fields, such as information and communications technology, biomedical diagnostics, global environmental monitoring, homeland security, quality, and process controls. Most of these applications require systems with targeted sensitivity and resolution exploiting advanced devices and optical components making use of novel materials and architectures. To address the above requirements, high-power sources with controlled and directional beam profiles, new optical components and highly efficient nano-detectors are needed. We here provide an overview on our recent developments in the field of 2D and 1D THz laser resonators, nano-detectors and passive components.

Quantum cascade lasers (OCLs) operating at THz frequencies have undergone rapid development since their first demonstration. Typically, continuous-wave (CW) operation is required to target application needs, combined with a low divergent spatial profile in the far-field, and a fine spectral control of the emitted radiation. This, however, is very difficult to achieve in practice when both single-mode emission and multimode emission are required. We recently demonstrated a novel distributed feedback wire THz QCL, in which feedback is provided by a lateral sinusoidal corrugation of the cavity, defining the emission frequency, combined with an array of holes in the top waveguide metallization, used for light extraction (Fig. 1a, 1b). This new architecture overcomes all the present technological limits in optimizing the performance of THz QCLs, and has led to the achievement of low-divergent beams (10°) (Fig. 1c), single-mode emission, very high slope-efficiencies (250 mW/A), and stable CW operation. Simultaneously, we also devised novel broadband coherent light sources; a random THz laser embedding a OCL heterostructure (Fig. 1d) capable to generate coherent broadband radiation combined with an almost diffraction limited far-field emission profile and~80 mW of optical power (Fig. 1e). In parallel, we also worked on the development of novel passive and active optical components. THz saturable absorbers (SA) can be extremely appealing in combination with OCLs to passively mode-lock these micro-sources. We developed flexible THz SAs by transfer coating and inkiet printing single and few-layer graphene films prepared by liquid phase exfoliation of graphite (Fig. 2b), achieving a record transparency

Fig. 1

(a) Schematic diagrams of the laterally corrugated wire laser with a periodic sinusoidal corrugation. (b) Scanning electron microscope (SEM) image of a fabricated device, having average width of 40 µm. (c) Far-field emission patterns measured at 20 K whilst driving the devices in continuous wave. (d) SEM image of a fabricated random laser. (e) Voltage-current density (V-J) and power-current density (L-J) characteristics of the random laser shown in panel (d) measured as a function of the heat sink temperature.


modulation of 80% at 3 THz (Fig. 2a). Furthermore, we devised lightning-fast switch for electron waves in the far-infrared based on black phosphorus (BP) heterostructures, in which interface polaritons can be activated by photo-induced interband excitation within 50 fs, with switching times on the femtosecond scale (Fig. 2d), many orders of magnitude faster than the fastest existing transistors. Finally to target the application need of near-field microscopy we devised near-field probes that exploit the inherently strong evanescent THz field arising within a sub-wavelength aperture. The latter originally coupled to asymmetric electrodes, activates the thermo-electric THz detection mechanism in a transistor channel made of flakes of BP or InAs nanowires. We then demonstrated room-temperature sub-wavelength resolution coherent imaging with a 3.4 THz QCLs (Fig. 2d). Finally, by exploiting the inherent electrical and thermal in-plane anisotropy of a flexible thin flake BP, we proved that it is possible to engineer THz nano-detectors exploiting hBN/BP/hBN van der Waals heterostructures, with integrated nano-antennas in which the detection dynamics can be designed from scratch. The achieved selective detection (40 V/W responsivity) and sensitivity performances (signal-to-noise ratio of 10000), can be exploited for real-time THz imaging in a realistic setting.

Fig. 2

(a) z-scan normalized transmittance of a water-based graphene saturable absorber probed with a 3.4 THz QCL. (b) Transmission electron microscopy images of few-layer graphene flakes from water based inks. (c) Scattered near-field intensity images of the SiO_/BP/SiO_ heterostructure, plotted for different delay times between the pump and probe pulses. (d) Profile of the detected photovoltage $\Delta u_{sD'}$ normalized to the total THz input power, in presence of two sharp needles in the vicinity of the aperture (inset). The detected signal reveals a spatial resolution of 17 µm evaluated as the FWHM of the peak. Inset: 2D color plot of $\Delta u_{sD'}$



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Tracking the coherent generation of polaron pairs in conjugated polymers

The optical excitation of organic semiconductors generates charge-separated polaron pairs with high yield. The microscopic mechanisms underlying such generation have been debated for many years. Here we use ultrafast two-dimensional electronic spectroscopy to study the polaron pair formation in a prototypical polymer thin film on a fs time scale. The measured spectra show pronounced peak splittings revealing that the optical excitations of this polymer are hybridized exciton-polaron-pairs, strongly coupled to a dominant vibrational mode. Such coherent vibronic coupling induces ultrafast polaron pair formation, accelerates the charge separation dynamics and makes it insensitive to disorder. These findings open up new perspectives for tailoring light-to-current conversion in organic materials.

Thin films of conductive polymers are key active materials for flexible organic optoelectronic devices such as solar cells, field effect transistors or light-emitting diodes. Their optical excitation not only results in the formation of excitons (Xs), but also in the creation of a wealth of other quasiparticles. Polaron pairs (PPs) are charge-neutral excitations in which spatially separated electrons and holes weakly interact via their Coulomb attraction and are each coupled to their own lattice distortion. They are thought to act as precursors of free charges, and are thus of fundamental importance for the efficient light-to-current conversion in polymer-based photovoltaic devices. Excitons and PPs are simultaneously created within the time resolution of the experiment, typically few tens of fs. Recent theoretical work suggests that strong vibronic coupling may lie at the origin of this efficient PP formation. Such a picture would underpin emerging experimental and theoretical evidence that vibronic couplings are important for photoinduced energy and charge transfer processes in biological and artificial light harvesting systems or organic solar cells at room temperature.

Here, we use 2D electronic spectroscopy with 10-fs temporal resolution to dynamically probe PP formation in annealed regioregular (rr-) P3HT thin films at room temperature. We compare our experimental results to quantum-mechanical simulations of 2D maps based on a dimeric version of the Holstein Hamiltonian. This includes a coherent coupling between the X and PP states, modulated by the vibrational mode. In the model simulations, dephasing and relaxation processes are described by a master equation in the Lindblad form. In spite of its simplicity, the model reproduces and allows us to interpret the main features observed in 2D maps. These include well defined spectral peak splittings, ultrafast appearance of the photoinduced absorption from the hybrid X-PP states, and multi-frequency oscillations of the peaks as a function of the waiting time, which represent clear signatures of strong vibronic coupling between excitons, polaron pairs and a dominant underdamped vibrational mode of the polymer. These results suggest that vibronic couplings might accelerate ultrafast polaron pair formation in organic materials, thus triggering the charge-separation dynamics on a fs time scale.

Two-dimensional electronic spectroscopy of annealed rr-P3HT thin films. The system is excited by a sequence of two fs laser pulses (pump) and probed by a third fs pulse. delayed by a variable waiting time (here 2.3 fs). The reported quantity is the differential transmission ($\Delta T/T$), given by the difference between the transmission measured with and without the pump pulses. In the 2D map, the differential transmission is plotted as a function of the excitation and detection energies. The positions of the peaks (marked with blue circles) are assigned, through the simulation of the 2D maps, to four hybrid exciton-polaron-pair states, labeled $|XP_{\lambda}\rangle$ to $|XP_{\lambda}\rangle$. The splittings between these peaks are the characteristic signature of strong vibronic coupling. Red corresponds to spectral regions where transmission is higher ($\Delta T/T>0$) in the presence of the pump pulses, which induce a bleaching of the



excitonic transitions. Blue regions ($\Delta T/T<0$) denote the occurrence of photoinduced absorption from the exciton-polaron-pair states, which we observe already at the shortest waiting times that can be experimentally accessed. At longer waiting times (not shown here) the splitting along the detection energy washes out. At all waiting times, negative amplitudes are observed for detection energy around 1.89 eV, monitoring polaron pair dynamics.

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Highlights -Solid-state quantum technology

Introduction to Solid-state quantum technology

Research on solid-state quantum technology is devoted to the investigation of quantum systems and phenomena, with the aim of developing novel ideas and concepts with a major impact on future quantum devices. The work, mostly based on low temperature magneto-transport techniques, addresses four main application domains, which are outlined in the following.

A crucial goal in quantum technology is to find ways to encode and manipulate quantum information in a robust fashion. This requires that sources of decoherence are suppressed, thus solving one of the main obstacles for the implementation of quantum information processing. This is at the heart of the study of topological states of matter and strongly coupled quantum states. Activities at Cnr Nano on topologically-protected quantum systems include: Majorana bound states in semiconducting nanowires; electronic phases with nontrivial topology in core-shell semiconductor nanowires; non-local entanglement in Cooper pair splitters and in superconducting quantum interferometers; edge states in the quantum Hall regime and topological insulators; single-photon detectors based on topological meta-materials and hybrid photon-spin systems in the strong coupling regime, strong coupling between magnetic molecules and superconducting resonators.

The goal of the emerging field of coherent caloritronics (**heat control and manipulation**) is to design and implement thermal devices that can control energy transfer with an unprecedented level of accuracy and velocity, complementing state-of-the-art electronic devices with novel functionalities and better effi-

ciencies. Work at Cnr Nano focuses on: the control of individual spins in nanowire-based quantum dots or single molecules, with a particular focus on quantum thermometry and heat engines; quantum thermodynamics and design of efficient quantum machines; coherent control of heat in nanostructures and local temperature sensing.

Electron spins are prototypical examples of two-level quantum systems, and are thus well suited for the implementation of quantum bits. A physical realization of such spin qubits currently investigated at Cnr Nano is based on the use of magnetic molecules. Work on **molecular spin qubits** focuses on the electrical addressing of single molecular spins in spin-transistor devices. Following an alternative route, molecule spins can also be coupled to photons in the confined modes of superconducting cavities, which represents a fundamental step for the coherent transfer and the manipulation of the spin state and for the implementation of hybrid quantum devices.

Quantum metrology employs quantum mechanical effects for setting the standards that define units of measurement and for other high-precision measurements. This field strives to develop measurement techniques that enhance precision beyond that possible through classical approaches. Cnr Nano researchers work on graphene quantum Hall resistance standards, on strain engineering to achieve Landau quantization even in the absence of a large magnetic field, and on hybrid superconductor/normal metal coherent devices for new current standards.

Activity Report 2018

Topology in hybrid and multi-terminal Josephson junctions

Topologically protected systems have an enormous potential impact on quantum technologies, especially for quantum computation purposes. Much attention was devoted to topological superconductivity and Majorana bound states (MBS), which are generated in hybrid platforms between semiconductors and superconductors with broken time-reversal. We have explored both experimentally and theoretically possible signatures of topological transitions in those systems. We also propose an alternative route to encode the topological protection in superconducting multiterminal Josephson junction nanodevices based on the proximity effect. Here, tunneling conductance fully reflects the expected topological protected quantum computation protocols.

Big expectations revolve around the MBS-based topological quantum computation. A convenient experimental platform is a hybrid systems obtained by semiconducting nanowires proximized with superconductors under a magnetic field. There, it is particularly important to identify when the system undergoes a topological transition creating MBSs at the boundaries. At Cnr Nano we investigated systems made of InAs nanowire multiterminal Josephson junctions (Fig. 1a). We have identified an unexpected increasing of the critical current with magnetic field, as a possible signature of the topological transition (Fig. 1b). This result agrees with the theoretical models which also predict peculiar jumps in the current-phase relationship (Fig. 1c).

Hybrid devices based on superconducting proximity effect in multiterminal configurations offer also another opportunity to engineer topological non-trivial quantum states. We have realized the first double-loop Josephson interferometer with three terminals (Fig. 2a) based on a proximised weak link and probed its characteristics by means of tunneling spectroscopy. This structure promotes an additional phase control and allows an exotic phase-engineering of the weak-link topology which manifests in the behavior of the interferometer conductance.

Varying the phase differences between the three arms of the interferometer we observe transitions between gapped (insulating) and gapless (conducting) regions. The topological numbers characterizing such gapped states are given by superconducting phase windings over the two loops forming the Josephson interferometer. Since these gapped states cannot be transformed to one another continuously without passing through a gapless condition, they are topologically protected, demonstrating their non-trivial nature. The density of state of the three-terminal devices is accessed through a metallic tip tunnel-coupled to the weak link. Transitions between gapless and gapped regions are revealed by measurements of the tunneling conductance as a function of voltage bias and magnetic flux (Fig. 2b and Fig. 2d). Comparison with theoretical calculations fully confirms the mentioned scenario (Fig. 2c and Fig. 2e). We have shown that the spectral properties are a useful tool to identify transitions between gapless and gapped states in this three-terminal setup. The induced supercurrents in the different arms are discussed, showing that these can be an alternative hallmark to the density of state of the topological properties.



Fig. 1

(a) False-color tilted scanning electron micrograph of the sample: InAs nanowire (green) connected in multiterminal Josephson junction with Ti/Al leads (violet). (b) Nanowire based Josephson junction I-V characteristics as a function of the magnetic field measured in mT (each curve is horizontally shifted for clarity); unexpected increasing of the critical current at 24mT signals the topological transition from trivial to non-trivial phase. (c) Theoretically calculated current-phase-relationship I_j(ϕ) using tight-binding approach for different magnetic fields (different colors); discontinuities signal the topological transitions, showing that non-trivial phase has higher critical current than trivial phase.



(a) The ω -SQUIPT, three-terminal double-loop Josephson interferometer based on the proximity effect. False-color tilted scanning electron micrograph. The inset highlights the core of the interferometer: a nanosized T-shaped proximized Cu weak link (magenta) in a clean metallic contact with two Al superconducting loops (blue). Loop area is around 2 μ m². (b)-(e) Comparison between the tunneling conductance G vs V_{bias} measured at 30 mk (left panels) with theory (right panels) for symmetric (b and c) and asymmetric (d and e) length of the arm.

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Coherently coupling molecular spin centers to microwave photons: first steps towards integration of molecular spin qubits into superconducting circuits

Electron spins are ideal two-level quantum systems that can be coherently coupled to microwave photons in a cavity. This represents a fundamental step for developing quantum technologies based on hybrid solid-state devices, allowing for coherent transfer of quantum information between spins and other solid-state registers or flying qubits. We have first developed and optimized high- T_c superconducting coplanar resonators for experiments in a broad range of temperature and magnetic field. Then, we have systematically investigated different families of molecular spin centers, identifying the optimal parameters to achieve strong coupling with cavity photons.

Circuit Quantum Electrodynamics (circuit-QED) experiments are usually carried out by means of conventional superconductors like niobium or aluminum, which offer well-established procedures for the realization of planar superconducting circuits working in the mK temperature range. High-T_c superconductors, such as YBCO films, offer some peculiarities, such as superconducting transition at liquid nitrogen temperatures (T_c > 87 K), resilience in high magnetic field, and high power handling capability. These characteristics make YBCO resonators ideal platforms for investigating the coherent coupling of solid-state two-level systems with microwave photons in unconventional working conditions.

Molecular spin systems offer the possibility to tailor the magnetic interactions and the decoherence times at synthetic levels, while their processability on surfaces and integration on a nanodevice has been demonstrated for different nano-architectures. We have studied the magnetic dipolar coupling of several kinds of single-ion molecular spins with the fundamental mode of an YBCO resonator (Fig. 1) [1]. Vanadyl phthalocyanine molecules, in particular, show relatively long decoherence times in a broad temperature range, allowing observation of Rabi oscillations at room temperature for dispersions of VOPc molecules in a non-magnetic TiOPc analog. Our transmission spectroscopy experiments have shown the achievement of the high cooperativity regime for a 10% VOPc: TiOPc dispersion at 0.5 K (Fig. 2) [2].

Spin ensembles of organic radicals are characterized by high spin densities and sharp spin transitions due to the presence of weak intermolecular exchange interactions. We studied PyBTM organic radicals reporting a coupling strength of 95 MHz, which is much larger than the spin linewidth of 7 MHz and the cavity decay rate of 0.3 MHz (Fig. 2c). With these numbers, the cooperativity reaches 4300 at 2 K [3]. This has allowed us to study the hybridization of the spin modes of physically separated spin ensembles, coupled through cavity photons in a YBCO superconducting resonator (Fig. 2d).



Pictorial representation of a vanadyl phthalocyanine spin ensemble coupled to a superconducting YBCO/sapphire coplanar resonator. The spin centers are positioned in the middle of the resonator in correspondence to the antinode of the magnetic component of the microwave field (B_{η}) . The applied magnetic field (B_{η}) is used to tune the Zeeman energy of the spins, allowing for the coupling with the resonant cavity photons.

Fig. 2

Transmission spectroscopy of molecular spin ensembles coupled to a YBCO / sapphire coplanar resonator. (a) Hyperfine splitting of the doublet transition of a 10% VOPc:TiOPc dispersion in the weak coupling regime (T=1.5 K). (b) Transmission spectral map measured at T=0.5 K showing the achievement of the high cooperativity regime [2]. (c) Rabi splitting obtained with a PvBTM organic radical ensemble of ~1017 spins. The large anticrossing corresponds to a coupling strength of 95 MHz (T=2 K) [3]. (d) Cou-



pling of two PyBTM and DPPH spin ensembles. The multiple anticrossing indicates the hybridization of the spin modes located in physically separated ensembles [3].

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Heat mastering, thermal logic, and thermal memories in coherent caloritronics

Phase-coherent caloritronics takes advantage of long-range phase coherence in superconducting condensates to manipulate heat currents in solid-state mesoscopic circuits. The fundamental idea is to exploit suitable physical effects that depend on the superconducting phase difference φ , in order to control the electronic heat flow between two thermal reservoirs residing at different temperatures. Recently the group focused on mastering with unprecedented precision heat currents exploiting, e.g., a $0-\pi$ phase-controllable thermal Josephson junction (JJ). With the aim to realize thermal computing, the group proposed and theoretically demonstrated heat logic and thermal memory architectures.

The last experimental achievement of the group [1] in coherent caloritronics is a $0-\pi$ phase-controllable thermal JJ [2]. The latter is embedded in a superconducting quantum interference device (SQUID) containing three JJs (Fig. 1-a), one of which (j) supports a lower Josephson critical current than the others (a and b). This configuration enables the phase-biasing of (j). When the magnetic flux threading the SQUID ring is varied from 0 to $\Phi_0/2$, ϕ_j ranges from 0 to π , namely, a result achieved for the first time in a coherent caloritronic device. As a consequence, unprecedented temperature-modulation amplitudes (~100mK at $T_{bath}=25mK$, see Fig. 1-b), high magnetic sensitivities, and a remarkably high operational temperature up to 800mK are obtained.

The advent of heat transistors and thermal memories could pave the way to a new field called thermal logic, where information is transferred, processed, and stored in the form of thermal energy. The group theoretically demonstrated the first fully thermal caloritronic device based on an efficient thermoelectric hybrid junction coupled to a proximity heat valve: a very efficient temperature amplifier [3]. When the input temperature $T_{in}>T_{bath}$, a thermoelectric current flows through a closed circuit including a superconducting coil, whose flux controls the thermal current across the heat valve. While maximum and minimum values of the output temperature T_{out} depend on T_{bath} and T_{supply} , the value of T_{in} corresponding to the maximum T_{out} decreases as the inductive coupling is raised (see Fig. 2-a). This device can provide T_{out} values in the same range as T_{in} , thus representing a crucial element for the realization of thermal logic gates.

Moreover, we theoretically discussed the other fundamental block for a thermal logic: a superconducting thermal memory that exploits the thermal hysteresis in a flux-controlled, temperature-biased SQUID with a non-negligible inductance of the superconducting ring [4]. This system reveals a temperature bistability, which can be used to define two distinct logic states.

(a) Pseudo-color scanning electron micrograph of the 0-p Josephson junction. The S1 electrode, depicted in a yellow-red gradient, is coupled to five superconducting probes P. (i =1,2,...,5) and to the lower branch of the SQUID P. (S,, represented in blue). On the right side, S, is connected to the superconductor S₂ (also in blue). P, and P, are used as Joule heaters, whereas P_{x} , P_{4} , and P_{5} are used to measure the electrical properties of the interferometer and to probe the electronic temperature of S,. Inset: enlarged image of the SQUID, composed of three JJs.



(b) SQUID total switching current I_{sSQUID} versus magnetic flux ϕ piercing the loop of the interferometer for selected values of the bath temperature T_{bath}. The filled circles are experimental values, and the black lines are the theoretical fits.

(c) Calculated behavior of ϕ_j versus Φ for the supercurrent I=I_{sSQUID} flowing through the interferometer at T_{bath}=25mK.

(d) Calculated Φ_j versus Φ for I=0 and for the same parameters used in b. Dash-dotted line represents the calculated φ_a for the same parameters.



Fig. 2

(a) Schematic representation of the temperature amplifier: the thermoelectric element highlighted with the dashed rectangle is constituted of a metal (yellow), a ferromagnetic insulator (gray) and a superconductor (turquoise). The turquoise depicts the superconducting coil. The SQUIPT (red) is composed of a superconducting ring interspersed by a normal metal wire and a tunnel-coupled metal probe (orange) through a thin insulator (dark gray).

(b) Output temperature $\rm T_{out}$ as a function of $\rm T_{IN}$ calculated for $\rm T_{s}=250mK$ and for different values of Sens. The black dotted line represents the minimum value of active output $\rm T_{outputs}$. The output active range (OAR) is shown.

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We study the thermoelectric properties and heat-to-work conversion performance of an interacting, multilevel quantum dot (QD). At low temperatures, we derive analytical expressions for the transport coefficients which account for the interplay between interactions and level quantization. Formulas for the power factor and the figure of merit ZT for a QD-based heat engine are derived, identifying optimal working conditions which maximize output power and efficiency of heat-to-work conversion. Beyond the linear response, we find that output power and efficiency at maximum power can almost be simultaneously maximized by choosing appropriate values of electrochemical potential and bias voltage.

The study of thermoelectric effects in nanostructures is attracting increasing interest. Heat-to-work conversion based on thermoelectricity promises an enhanced efficiency as a consequence of the reduction of the phonon contribution to thermal conductance in disordered nanostructures and of the "energy filtering" effect that can result from confinement and quantum effects. A heat engine composed of a quantum dot (QD) is a paradigmatic example, since it is characterized by a spectrum of discrete levels which maximizes energy filtering.

Here we theoretically study the thermoelectric properties and heat-to-work conversion performance of a multilevel OD in a multi-terminal configuration within the Coulomb blockade regime. In the linear response and for low temperatures, we derive analytical expressions for all transport coefficients, for the power factor Q and for the figure of merit ZT (which controls the maximum efficiency and the efficiency at maximum power). We find the specific values of the gate voltage, which only depend on temperature, for which Q and ZT are simultaneously maximized, see Fig. 1. The regime beyond the linear response has been analysed numerically. In this case, the efficiency at maximum power develops peaks which approach the Carnot efficiency for large temperature differences. Remarkably, the maximum power, normalized to its peak value, only slightly depends on the temperature bias and can be well approximated by the analytic expression obtained for the linear response regime. Moreover, we find that efficiency at maximum power and maximum power take approximately their peak values simultaneously, under the same conditions found for the linear response. In conclusion, we find that Coulomb interactions dramatically increase ZT (by strongly suppressing the thermal conductance, see Fig. 2) and the non-linear-response efficiency at maximum power (pushing it above the Curzon-Alhborn limit). We are currently extending the approach developed here to analyse experimental data on QDs and metallic islands, to account for quantum coherence effects and multiple-QD energy exchanges.

(a) Power factor Q and (b) figure of merit ZT are plotted as a function of the electrochemical potential μ (gate voltage) for a multi-level QD. For both quantities, the analytical quantum limit is plotted as a red dashed curve, while the numerically calculated result is plotted as a black solid curve. All curves are calculated for a charging energy E_c =50 k_BT , level spacing Δ E=10 k_BT , and coupling energy of the tunnel barriers defining the QD given by $\hbar\Gamma$ =0.01 k_BT , T being the reference

temperature. Q* $\simeq 0.22 \frac{\Gamma k_B}{T}$ is the peak value $exp(\frac{\Delta E}{T})$

of Q, $ZT^{\star} \simeq 0.44 \frac{exp(\frac{\Delta E}{k_BT})}{(\frac{\Delta E}{k_BT})^2}$ is the figure of merit

peak value, and $ZT_{p}=3$ (for large p) is the value of ZT of the secondary peaks.





Fig. 2

Comparison between the thermal conductance K and K^(NI) of, respectively, an interacting (red dashed curve) and a non-interacting (black solid curve) QD, plotted as a function of the electrochemical potential μ . Both cases have been computed with the parameters used in Fig. 1, except for setting E_c=0 in the non-interacting case. The interacting thermal conductance has been multiplied by a factor 70. In particular, its maximum value is half the minimum of K^(NI).

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Addressing individual spins with molecular transistors

We present the realization and study of molecular spin transistors with different architectures. We monitor the Landau-Zener dynamics of a single-ion magnet inserted into a spin-transistor geometry in which a single TbPc₂ molecule is contacted by gold electrodes. The spin reversal probability, measured as a function of the field-sweep rate, displays clear deviations from that of a closed system. These are shown to result from a dephasing process, which is successfully simulated by means of an adiabatic master equation with time averaged Lindblad operators, and tentatively interpreted in terms of the finite time resolution of the continuous measurement. Following a complementary approach, we fabricate molecular transistors using graphene electrodes, showing that the use of graphene represents a promising way of addressing single molecules.

Molecular spin transistors represent a novel class of devices, where an individual magnetic molecule is contacted by source-drain electrodes in a three-terminal (transistor-like) configuration. They are an effective way to address and control molecular spins, and are considered promising in the field of quantum technologies. At Cnr Nano we focus on the realization and study of single molecule transistors made with TbPc, single ion magnets, using different architectures. Employing a more "traditional" geometry depicted in Fig. 1, in which an individual molecule is contacted by gold electrodes, we study how the continuous measurements affects the dynamics of the molecular spin, while this is driven through an avoided level crossing (Landau-Zener problem) and continuously measured by the current that flows through the molecule. Here, we experimentally and theoretically investigate the deviations that environment- and measurement-induced decoherence induces in the spin dynamics (and, more specifically, in the spin-reversal probability P), with respect to the case of an isolated system. The weak dependence of P on the initial (ground or excited) spin state indicates that the spin is affected by dephasing, rather than relaxation or incoherent excitation. Besides, rather counterintuitively, deviations from a coherent behavior are more significant for high field-sweep rates than for slow spin dynamics. In order to account for the experimental results, we simulate the spin dynamics through a phenomenological master equation, with time-averaged Lindblad operators. The simulations suggest that the form of dephasing affecting the spin depends on the time scale of the Landau-Zener process and explains why decoherence becomes less effective in the limit of an adiabatic time evolution. In the case of a measurement-induced dephasing, the time average of the dephasing operators can account for the finite time resolution of the continuous measurement.

Alternatively, we develop a molecular device where graphene is used as the sourcedrain electrode material, see Fig. 2. Graphene is considered a promising material for fabricating stable molecular-scale electrodes. By realizing nanometer spaced electrodes and employing the so-called feedback controlled electroburning, we demonstrate a molecular device in which we can measure the strength of the magnetic exchange coupling between the electronic spin of the Tb³⁺ magnetic core and the current passing through the molecular system in the Coulomb blockade regime. It is this exchange coupling that allows the possibility to read out both the electronic and the nuclear spin state of the Tb ion electrically, i.e., by means of conductance measurements.

Fig. 1

(a) Artistic view of the molecular spin transistor with the magnetic molecule (TbPc₂) embedded between the gold electrodes. (b) Schematics of the molecular system: one of



the phthalocyanine ligands acts as a read-out quantum dot, where the spins of the localized electrons are exchange-coupled to the total angular momentum (J=6) of the Tb^{3+} ion, whose $M_3=\pm 6$ states are well separated in energy from the remaining ones, and thus define an effective $\frac{1}{2}$ spin. The molecule is driven through an avoided level crossing by a time-dependent magnetic field and undergoes a spin reversal, which is experimentally detected by monitoring the spin-dependent current that flows through the molecule.

Fig. 2

(a) Artistic picture of the molecular transistor realized with graphene-based electrodes. (b) Color scale map of the differential conductance dl/dV measured as a function of the source-drain voltage



 V_{ds} and of the applied magnetic field B. An antiferromagnetic exchange coupling between the current flowing through the molecular quantum dot and the Tb³⁺ electronic spin can be deduced, with a coupling constant corresponding to a magnetic field of about 1.10 T.

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Starting from high quality CVD-grown single crystal graphene we fabricated both Hall-bars and Quantum Point Contacts which we extensively studied in the Quantum Hall (QH) regime showing full control over backscattering and equilibration of the topologically-protected edge states. Strain engineering was also explored as an alternative and original method to modify the electronic properties and induce quantizing pseudomagnetic fields. To this end, we pulled free-standing graphene membranes and studied strain using micro-Raman. Finally, we observe weak localization features in black Phosphorus from which information about elastic and inelastic scattering length is a signature of the in-plane crystalline anisotropy in black Phosphorus.

Quantum Hall effects offer a formidable playground for the investigation of quantum transport phenomena. Our low-temperature magneto-transport data show more than 12 flat and discernible half-integer quantum Hall plateaus in single-crystal CVD graphene samples on both the electron and hole sides of the Dirac point [1]. We furthermore demonstrate a buried split-gate architecture with this material. The control of the edge trajectories in these devices is demonstrated by observation of various fractional quantum resistances, as a result of a controllable inter-edge scattering. Our architecture is particularly promising and unique in view of the investigation of quantum transport via scanning probe microscopy, since graphene constitutes the topmost layer of the device [2].

The unique electronic properties of graphene can be strongly influenced by a mechanical deformation of its carbon lattice. For peculiar strain profiles, it is possible to induce an effect which is equivalent to a quantizing magnetic field having two opposite signs for the two Dirac cones. We demonstrate a novel method to obtain a custom strain profile by depositing graphene on a patterned SiN membrane and by applying a differential pressure load (see Fig. 2). We show in particular that a uniaxial deformation can be obtained for elliptical holes [3]. The strain induced on the graphene flake is studied by micro-Raman spectroscopy of the G and 2D peaks and based on a comparison with finite element models. Using simulations, we identify suitable architectures for the observation of pseudomagnetic fields.

Weak localization was observed in a black phosphorus field-effect transistor, see Fig. 3, in excellent agreement with the Hikami-Larkin-Nagaoka model, from which characteristic scattering lengths could be inferred. The temperature dependence of the phase coherence length L ϕ was found to decrease weaker than expected for two dimensions. Rather, the observed power law was found to be close to that observed previously in quasi-one-dimensional systems such as metallic nanowires and carbon nanotubes.

We attribute this more robust character of $L\varphi$ to the highly anisotropic nature of the puckered honeycomb crystal structure of bP [4]. Ongoing work focuses on the functionalization of exfoliated bP [5].



Landau fan diagram, in which the longitudinal resistance R_{xx} across the split gate is plotted as a function of back gate voltage V_{BG} and magnetic field B. More than 12 Landau levels can be seen in this diagram, indicated by their respective index. Color scale gives log(R_{xx}). Temperature T = 250 mK.

Fig. 2

Unaxially strained graphene. (a) A graphene flake deposited on a SiN membrane with an elliptic hole is subject to a differential pressure load DP. (b) Average strain is detected by measuring the local energy shift of the Raman peaks: the G peak shift is visible in the panel. (c) The presence of an anisotropic strain component induces a splitting of the two G+ and G- phonon modes.





Fig. 3

Weak localization measurements. (a) The characteristic weak localization peak is observed in a plot of the normalized longitudinal resistance (R_{xx} (B) – R_{xx} (0))/ R_{xx} (0) versus magnetic field B and gate voltage V_{a} at T = 0.26 K.

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Highlights -Surfaces and interfaces: nanofabrication, imaging, and spectroscopy

Introduction to Surfaces and interfaces: nanofabrication, imaging, and spectroscopy

The Institute activities concerning **surfaces and interfaces: nanofabrication, imaging, and spectroscopy** point at optimizing important functionalities in materials through an atomic scale understanding of the modifications introduced by confinement. The materials are produced in the Institute laboratories and controlled through the combination of high resolution spectroscopies, microscopies and theoretical simulations. The activities are performed also at shared facilities, like synchrotron radiation sources and transmission electron microscopes. An important piece of activity concerns in particular the development of analysis techniques based on electron vortex beams.

Graphene-based materials with tunable electronic, optical, structural, and mechanical properties are developed and manipulated in view of the application in different fields. An interesting possibility is given by the use of graphene for hydrogen storage. In this context the Institute activities have shown that the hydrogen storage capacity of the material can be enhanced by the rippling induced by the interaction with specific substrates and by the presence of metal clusters. Light-weight metal intercalation is also favored by the corrugation. In graphene nanoribbons, extraordinarily versatile semiconducting materials, the optical and electronic behavior of each atomic species has been identified, opening the way to promising applications in nanoelectronics and optoelectronics. Moreover, the unique mechanical properties of graphene have been exploited in view of the development of efficient ultrathin lubricant and antiwear coatings. In this context the mechanisms which induce a lower friction on realistic and extended graphene coatings have been investigated.

Researches concerning the development of defect-free **nanowire semiconductor heterostructures** focused on the understanding

of nanoparticle-nanowire interactions during the metal-assisted growth. The activities, involving high-resolution imaging and modelling, lead to important results towards the achievement of a full control over the morphology and the properties of the systems.

The activities concerning **oxide-based systems** focused on transparent conducting and reducible oxides, of interest for energy and environmental applications. In transparent conducting oxides the optical and electronic modifications induced by highly diluted elements and by the additional defect species have been identified. In reducible oxides the proximity of metal species, reduced dimensionality and defect distribution have been shown to largely influence the reducibility, a property on which the diverse applications of the material are based.

Flexible piezoelectric materials enable ultra-high pressure sensitivity and integration in accelerometers and nano-generators. The Institute activities focused on the understanding of the nanoscale interactions responsible for the piezoelectric mechanisms in individual polymeric nanowires and on the realization of more complex light-emitting systems.

Recent important results on the application of large orbital moment **electron vortex beams** concern the development of innovative methods for the measurement of magnetic fields. The Institute researchers exploited their first observation of the vertical Aharonov-Bohm effect as a new approach to quantify the longitudinal component of magnetic fields. To determine the transverse component, they developed a method which converts the magnetic phase into an amplitude by a unitary transformation of the wave function, achieved through new holographic elements. Graphene's exceptional structural and mechanical properties make it potentially applicable in many high tech fields, especially those related to energy and environmental applications. Cnr Nano activity in the last two years was involved in fundamental studied related to the possibility of using graphene in energy storage devices. These require in any case some sort of manipulation. For instance, Hydrogen storage via chemisorption was shown to be enhanced by rippling on SiC due to interaction with the substrate; Hydrogen adsorption can be mediated by transition metal clusters such as Ti. Finally, Li intercalation was also considered as a possible way to functionalize graphene because light-weight metals mediate H_2 adsorption, or to use graphene in batteries.

In this decade after its first observation, it has become clear that for most applications graphene needs some sort of manipulation [1]. Substitutional doping can increase the density of carriers, while any kind of defects (substitutional, structural, or adatoms) can be used to open the band gap. Both of these features are needed for applications in nano-electronics. In the field of substance storage for energy applications (e.g., hydrogen storage or electrolytes adsorption), the problem is the low physisorption level of graphene, which can be enhanced either by structural manipulation (curvature, creation of porosity), or by decorating graphene with metals. Finally, the manipulation of the local reactivity is important for the chemical functionalization with anchor molecules, useful to attach pillars for building 3D superstructures [1].



Fig. 1

Graphene monolayer on SiC(0001) with different corrugation patterns color-coded according to height (red protrusion, blue intrusion) as obtained with DFT simulations of the monolayer model system including the full symmetry of moiré pattern and 4 layers of substrate (~1800 atoms). Configurations are evaluated with different functionals (LDA, PBE, and PBE-D2, as indicated) and differ between each other by ~0.2-0.6 eV. In the lower row, the configuration of the buffer layer is also reported (black to grey, protrusion to intrusion), displaying a more pronounced corrugation and more evident moiré pattern. The structural profile of buffer and monolaver with different functionals is reported in the plot.

Our idea is to exploit the natural corrugation of graphene grown on SiC to enhance one or more of the mentioned features. The moiré pattern of corrugation is multi-stable (see Fig. 1) and can be manipulated by changing environmental conditions [2] (e.g., temperature, external fields). This in turn opens the possibility of manipulating reactivity, which is shown to be larger on convexities. Corrugation and other kinds of structural defects can favor the adhesion of metal clusters (e.g., Ti). This increases the adhesion of hydrogen, both in atomic and molecular form, capable of different kinds of binding modes with the Ti clusters [3]. Finally, graphene on SiC was shown capable of efficiently adsorbing Li by intercalation (see Fig. 2), opening the possibility of applications for batteries [4]. The future developments of these studies include their extension to – less ideal but more feasible – nanoporous graphene, a widely studied material currently considered the most viable 3D version of graphene.



Fig. 2

(a) STM topographical image taken after deposition of 0.031 ML Li on. In the middle there is a flat and not reconstructed region which is identified as the Li-intercalated region. Scan area: 50 x 50 nm². (b) STM topographical image taken after deposition of 0.047 ML Li. The image shows that the Li-intercalated area has grown as compared to (a). The images suggest that Li-intercalation starts from the step edges of the substrate. Scan area: 72 x 72 nm². (c) Magnification taken from the area indicated by the solid square in (a). Scan area: 20 x 20 nm². (d) Cross-sectional plot taken along the black line in (c). From the step height we can calculate by how much the graphene film is lifted up by the Li-intercalation. Image parameters: (a)-500mV, -170 pA; (b) 1 V, 1 nA; (c) -500 mV, -170 pA.

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Fingerprinting atomically precise graphene nanoribbons: from fundamental properties to devices

Amongst organic electronic materials, graphene nanoribbons (GNRs) offer extraordinary versatility as next-generation semiconducting materials due to their tunable charge-carrier mobility, optical absorption and electronic bandgap, which are all controlled by both the quantum confinement and the specific atomic structure. We here show how, combining ab-initio simulations with spectroscopic and photoconduction measurements, we can selectively fingerprint the peculiarities of each GNR species, in terms of both atomic structure and morphology as well as optical and electronic behavior. These results open the way to future applications in the nanoelectronics and optoelectronics fields.

Bottom-up synthetic approaches to the fabrication of graphene nanoribbons (GNRs) guarantee an atomically-precise design of GNR width and edge pattern, allowing for an on-purpose tailoring of their properties and functionalities. We combine theoretical and experimental investigations on structurally different GNRs, i.e. *chevron-type* and *cove-shaped*, which allow us to draw a comprehensive picture of their vibrational and optoelectronic properties as resulting from structural specificities.

The comparison of Raman [1] and HREEL [2] spectroscopy with ab-initio simulations shows that GNR width, edge and termination morphology, and functional groups all influence the GNR vibrational properties. For both techniques, the low-energy spectral region is particularly sensitive to morphology and functionalization, while the Raman D peak dispersion can be used to uniquely fingerprint the presence of GNRs and differentiates them from other sp² carbon nanostructures. Theoretical simulations of IR and optical spectroscopies also reveal, in agreement with experimental findings, that strain-induced non-planarity arising from edge functionalization results in a controlled modification of both fundamental and optical gaps, thus paving the way toward a fine-tuning of GNR properties by purely-structural effects.

Furthermore, the use of different spectroscopies, ranging from EELS and RDS [3] to femtosecond transient absorption spectroscopy [4], in combination with theoretical simulations including many-body effects, allows us to elucidate the nature of optical excitations, demonstrating the fundamental role played by excitons and biexcitons in determining the linear and ultrafast optical response of GNRs.

Finally, these GNRs have been used to realize the semiconductive channel of a novel type of field effect transistor (FET) device, where graphene is employed as the source-drain electrode [5]. These so called all-graphene devices show on/off current modulation up to 10^4 and high light sensitivity, which are promising for future optoelectronics applications.



a. Ball-and-stick model of the atomic structure of cove-shaped GNRs with different width, edge functionalization and GNR orientation. b. Acoustic region of the Raman spectrum of the GNRs shown in a., where the main feature is attributed to the radial-like breathing mode (RLBM). c, d. Density-functional Perturbation theory simulations of the vibrational properties allow us to understand the relationship of the RLBM position as a function of width (c) and edge functionalization (d). e. Ab initio simulation of the linear optical spectrum of selected cove-shaped GNR (4CNR, top panel in a), as compared to the experimental curve (theory is in blue, exp. in black). f. Femtosecond transient absorption spectroscopy of the 4CNR. The stimulated emission at about 650 nm is attributed to recombination of biexcitons forming by nonlinear exciton-exciton annihilation in the high-excitation regime. g. Tight-binding plus Quantum Monte Carlo simulations are employed to estimate the biexciton binding energy.

Fig. 2

a) Atomically-precise chGNR are grown on a gold surface by surface-synthesis. HREELS vibrational spectra clearly fingerprint the different steps of GNR formation (as schematically shown on the left). The shape of the CH wagging-mode manifold which dominates the chGNR spectrum (red curve) is compared with ab-initio theoretical simulation, providing detailed information on the chGNR edge and termination topology.

b) The optical excitation of the precursor polymer and of chGNRs are measured by RDS and HREELS and compared with ab initio calculations based on many-body perturbation theory. The dielectric function of precursor polymer (blue) and ch-AGNR (red), extracted



from the RDS and EELS data and fitted to a Lorentzian oscillator model results in very good agreement with that computed by Bethe–Salpeter equation. Positions and intensities of the fitted Lorentzian oscillator transitions are shown as vertical bars [2].

c) In our "all-graphene" devices (see scheme in the inset) graphene flakes are employed as the source-drain electrode material to contact a thin film of GNRs used as the conductive channel. As a representative example of the electrical behavior of the resulting FET, the measured I-V curves are displayed for different gate voltages. The devices show an n-type FET behavior with current on/off ratios as high as 10⁴. Remarkably, the GNR/graphene devices also show high light sensitivity, with the capability to detect signals as small as 10⁻¹⁵ W.

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Graphene is a natural candidate to be the thinnest solid state lubricant and antiwear coating. First, graphene derives from graphite, a well-known lamellar solid lubricant. Second, single layer graphene has shown unique properties like high mechanical strength, large stiffness, chemical inertness and stability. Experiments by Friction Force Microscopy (FFM) on ideal single layer graphene systems have confirmed this expectation. A large reduction of friction (from 10 to 15 times) with respect to silicon and metal oxide substrates has been measured in ambient condition. Now scientific and technical debate moves to verify and understand friction reduction on realistic and extended graphene coatings. Here we present results on two different systems, namely a commercial few layers graphene film grown by Chemical Vapor Deposition (CVD) on Nickel and graphene flakes deposited from liquid solution on iron.

Few-layer graphene (FLG) films grown by CVD on Nickel are composed by grains of variable layers thickness, usually less than 10, with lateral size of a few microns separated but connected by boundary regions (Fig. 1 a,b,c). We performed FFM experiments with nanometer contact size and load into the nanoscale regime and we measured a difference in friction response between grain regions and interfacial boundaries.

Friction coefficient on grains is higher with respect to interfacial boundaries and becomes negative in the negative load regime, i.e., when the tip is pulled-off from surface (Fig. 1 e). This last behaviour has been already observed when adhesion between tip apex and topmost graphene layer is higher than the exfoliation energy. Finite element simulations mimicking the experimental conditions identified the role of out-of-plane deformation in tuning the lateral force and friction in our system. Graphene frictional characteristics depend on its out-of-plane bending stiffness, which is in turn governed by graphene intra-layers interaction and graphene-Nickel adhesion. The availability of upper layers with limited interaction with the substrate, and thus with lower stiffness, leads to higher puckering, and consequently higher friction forces. Therefore, resistance to out-of-plane deformation for graphene coatings is the key element to minimize friction in nanoscale single asperity contacts.

An ethanol solution containing graphene flakes was used to lubricate a steel-iron and a steel-bronze interface in a macroscopic ball-on-disc friction tests. The reduction of friction coefficient due to graphene was compared to the one obtained with the use of pure ethanol and to the "dry" condition. A reduction of friction ascribable to graphene was measured both in terms of absolute value and in terms of duration compared to the pure ethanol.

The Raman spectroscopy performed on the disc surfaces and on the contact area of the balls showed that graphene flakes bind to iron rather than to other materials. Indeed, in the steel-iron sliding contact graphene was found on the Fe surface, while in the steel-bronze system graphene bound to the active regions of native iron which were produced on the steel ball by rubbing. We were therefore able to show that the lubrication due to the graphene flakes is related to the chemical passivation of iron by graphene as suggested by a recent theoretical work.

The differences between the friction coefficients obtained on pure iron and on bronze were attributed to the different coverage of the surfaces. In the case of steel ball sliding on bronze, the small contact area of the sphere is quickly covered by graphene flakes inducing a more stable and durable lubricating effect.



Fig. 1

Topology and friction map correlation for specific Gr/Ni-P region. a) Optical image ~15 × 15 μ m² of Gr/Ni–P showing a large grain region in the centre. b) SEM image of the same region (20 \times 20 μ m²). c) AFM topographic image $(15 \times 15 \,\mu\text{m}^2)$ measured in contact mode in air condition corresponding to marked region in panel (b). d) Overlapping of topography and friction map; the red colour represents areas characterized by friction force values between 10 and 30 nN: the remaining areas correspond to friction forces below 10 nN. e) Load-dependent friction curve obtained in vacuum (10⁻⁵ Torr) condition with silicon tip covered by native oxide. Green corresponds to grain region, red to boundary regions.



Fig. 2

Friction coefficient results. a) Example of the friction coefficient behaviour in a dry contact (black), in a contact lubricated by ethanol (blue) and in a contact lubricated by ethanol solution containing graphene (red). The arrows represent the application time when droplets are poured, the number of which is indicated by the arrow; b) Average values of the friction coefficient obtained averaging the data of the tests after the solution application.

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Nanoparticle stability for the growth of axial nanowire heterostructures controlled by catalyst composition tuning

The possibility to expand the range of material combinations in defect-free heterostructures (HSs) is one of the main motivations for the great interest in semiconductor nanowires (NWs). However, most axial NW HSs suffer from interface compositional gradients and kinking, as a consequence of nanoparticle-NW interactions during the metal-assisted growth. Understanding such interactions is fundamental to achieve a full control over the morphology and the properties of the NW HSs. We investigated the Au-assisted growth of InAs-GaAs and InAs-InP axial NW HSs and we found that the nanoparticle composition controls the growth mode and the resulting NW morphology. We developed a model that is capable of describing all the observed phenomena: straight growth versus kinking, stationary nanoparticle compositions and interface abruptness.

One of the greatest advantages of NWs is their ability to relax elastic stress in two dimensions. This feature enables defect-free growth in lattice-mismatched material systems and yields structures that are not achievable in thin films or Stranski-Krastanov quantum dots. However, obtaining straight junctions with sharp interfaces between the two materials in the vapor-liquid-solid (VLS) growth of axial NW HSs is still challenging.

We have shown that understanding the condition to preserve the stability of the alloy nanoparticle (NP) at the flux commutation, and optimizing the growth protocols accordingly, allows for the synthesis of straight single and double GaAs-InAs and InAs-InP NW HSs by Au-assisted chemical beam epitaxy (see Fig. 1).

The well-known problem of growing InAs on top of GaAs is solved by choosing the conditions that yield high group III content in the Au/In or Au/In/Ga NPs. This can be achieved by either growing short GaAs segments in double HSs or pre-depositing In before growing GaAs NWs in single HSs. The observed trend is related to the NP stability on the NW top, favored at large contact angles and hence high group III concentrations [1].

Furthermore, we demonstrate that the sole parameter affecting the growth mode (straight, tapered or kinked) of InP segments on InAs NW stems by the Au-assisted method is the NP composition. Indeed, straight untapered InAs-InP NW HSs are obtained only when the In/Au ratio in the NPs is low. Higher In/Au ratios yield radial extension at the NW top and finally the InP segment starts to kink. Tailoring the In/Au ratio of the NPs by varying the precursor fluxes at a fixed growth temperature enables us to obtain straight and radius-uniform InAs-InP NW HSs (single and double) with atomically sharp interfaces. Also in this case, the observed trend is related to the NP contact angle and stability. We developed a theoretical model which provides the conditions for NP stability and abrupt heterointerfaces for a rich variety of growth scenarios (see Fig. 2). Taking into account different NW/NP interfacial configurations

(forming wetting or non-wetting monolayers in vertical or tapered geometry), this generalized model allows to describe all the experimentally observed phenomena: straight growth versus kinking, the stationary NP compositions in pure InAs and In-As-InP NWs, the crystal phase trends, and the interfacial abruptness. Most importantly, our results can be extended to other material systems, providing a powerful tool for obtaining high quality axial NW HSs with well-controlled properties.



Fig. 1

False-colour SEM images of (a) single InAs/ GaAs NW HS, (b) single GaAs/InAs NW HS, (c) double InAs/GaAs/InAs NW HS, (d) double GaAs/InAs/GaAs NW HS, (e) single InAs/InP NW HS, and (f) multiple InAs/InP NW HS.

Fig. 2

Minimum surface energy landscape versus the contact angle for the model parameters of InP: vertical facets between points 1 and 2, widening between points 2 and 3, and kinking after point 3. Inserts show the representative TEM images of vertical InP segments on InAs for small contact angles (left), widening InP segments for intermediate contact angles (center), and kinked InP segments after passing the critical contact angle of about 115° (right).



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 Catalyst composition tuning: the key for the growth of straight axial nanowire heterostructures with group III interchange. V. Zannier, D. Ercolani, U. P. Gomes, J. David, M. Gemmi, V. G. Dubrovskii, and L. Sorba. Nano Lett 16, 7183–7190 (2016). Some of the properties of oxide based systems can be tailored to meet the requirements of potential applications by tuning the material composition through the addition of specific diluted species. Moreover, reduced dimensionality and defectivity play an important role in determining the material behavior. We discuss here two recent relevant case studies. Al-doped ZnO films have been shown to have tunable optoelectronic properties depending on the Al-doping concentration and on the additional defect species identified within the compound. A second example is cerium oxide in which metal proximity, spatial confinement and defect distribution have been shown to largely influence reducibility, a property on which most of the applications of the material are based.

An interesting opportunity in the field of oxide-based materials is given by the possibility to finely control the properties through an atomic scale understanding of the modifications induced by reduced dimensionality, defectivity and by introducing highly diluted metallic species within the crystal structure.

In transparent conducting Al-doped ZnO (AZO) films the dopant concentration largely determines the conductivity of the material and its optical properties. However, the different defects present in the material also have a non-negligible influence on its behavior. We proposed a method to accurately control the concentration of individual defect species like H ions, Zn vacancies, O interstitials, substitutional and interstitial Al atoms in the material. The method is based on the assignment of the nature of the features appearing in Hard X-ray Photoelectron Spectra (HAXPES) and in X-ray absorption near-edge structure to different atomic sites by comparison with Density Functional Theory (DFT) modelling (Fig. 1). Moreover, it was possible to relate the defect concentration to the oxide stoichiometry and to small lattice distortions [1].

To investigate the effects of metal proximity on the reducibility of cerium oxide we used resonant inelastic X-ray scattering at the Ce L_3 absorption edge on platinum-supported epitaxial films of different thickness. In ultrathin films a modification of the electronic properties compared to thick films has been identified and ascribed to a non-negligible decrease of surface oxygen vacancy formation energy [2]. The effects of dimensionality, surface morphology and defectivity on the reducibility have been investigated on cerium oxide mass-selected nanoparticles. We identified the distribution of different ionic species within the NP, and we correlated the defect distribution to oxygen transport properties in different kinds of nanoparticles, using Scanning Transmission Electron Microscopy in the Electron Energy Loss (STEM-EELS) mode (Fig. 2) [3]. Moreover, we detected a size-induced contraction of the Ce-O distance, expected to largely influence the properties of the material [4].


HAXPES O Is spectrum of an AZO film with 3.6 at% concentration of AI grown by magnetron sputtering. The three O Is components in green, orange, and blue have been ascribed to different O sites within the material by comparison with the DFT model, sketched on the right.



Fig. 2

STEM-EELS maps of the distribution of Ce³⁺ (red) and Ce⁴⁺ (green) ions for mass-selected cerium nanoparticles prepared using different growth procedures obtained by fitting with Ce M^{4,5} reference spectra. (a) Individual nanoparticle after post-growth oxidation in the deposition chamber, (b) individual nanoparticle obtained by direct oxidation in the aggregation chamber, and (c) nanoparticle agglomerate obtained by oxidation in high vacuum. The different distribution of Ce³⁺ ions is connected with the defect distribution and it influences the reducibility of the system.

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Piezoelectric and mechano-tunable polymer nanowires for energy-harvesting and strain sensing

Flexible piezoelectric materials, in the form of sheets of aligned nanofibers and individual nanobeams of poly(vinylidenefluoride) copolymers, enable ultra-high pressure sensitivity and integration in accelerometers and nano-generators. We investigated the piezomechanisms in individual nanostructures and realized more complex systems by doping with light-emitting molecules, unveiling mechanically-tuneable interactions at nanoscale which make the fiber emission sensitive to tensile stress.

Piezoelectricity is the capability of certain materials to generate spatially separated electrical charges of opposite sign, in response to an external stress. The accumulation of electrical charges at the opposite edges of the material body allows for the generation of a piezopotential and a stream of current flowing through an external circuit can be recorded (Fig. 1a) by establishing electrical contacts at the two ends of the material (Fig. 1b).

Electrospinning technologies, due to the combination of strong stretching forces and high electric fields, have allowed us to realize piezoelectric materials in the form of nanofibers and nanowires with enhanced piezoelectric properties. Individual suspended fibers of poly(vinylidenefluoride-co-trifluoroethylene) (PVDF-TrFE) with diameter 400–600 nm and length in the millimeter scale (length to diameter ratio up to 5×10^5), generate open-circuit voltage of 60 mV under well-defined levels of displacement in the submicroscale (30–100 nm, Fig. 1a). Density functional theory has been used to calculate the piezoelectric coefficients and the full piezoelectric tensor for different copolymer configurations, also highlighting the role of shear forces contributions in flexible polymeric nanobeams.

By doping the PVDF-TrFE with light-emitting molecules (Fig. 1c), an electromechanical coupling through piezoelectric polymer chains makes the nanofiber emission sensitive to tensile stress and enables a reversible tuning of the emission of the embedded organic molecules. A red shift of the rhodamine 700 emission up to 5 nm is found upon the application of dynamic tensile stress (~1.5 N/mm²) during bending experiments (Fig. 1d). These new photophysical properties are associated with mechanical stresses applied to electrostatically-interacting molecular systems, namely to counterion-mediated states which involve light-emitting molecules as well as charged regions of piezoelectric polymer chains. These electrostatic class of supramolecular functional stress-sensitive units may impart new functionalities in hybrid molecular nanosystems and anisotropic nanostructures for sensing devices and soft robotics.



(a) Measured output voltage under repeated load/unload cycles for the suspended nanobeams at different displacements: 38 nm, 48 nm, 109 nm, from bottom to top panel. (b) Scheme of the fabrication steps for piezoelectric devices based on suspended PVDF-TrFE nanobeams. Features not in scale. (c) SEM micrograph of composite nanowires based on PVDF-TrFE doped with the organic dye rhodamine 700. Scale bar: 10 μ m. (e) PL spectra from arrays of PVDF-TrFE/rhodamine 700 fibers during mechanical bending. Blue and red markers highlight the position of the PL peak at each time, while photographs capture the corresponding mechanics. Spectra are vertically shifted for better clarity.

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Electron beam shaping for unconventional magnetic measurements in TEM

Electron Vortex beams are among the most innovative and fascinating topics on electron microscopy for their connection to quantum optics and fundamental physics but at the same time they are interesting as a new tool in the characterization of materials.

Vortex beams are electron waves in free space but still characterized by a rotation around the propagation axis. The origin and the propagation behavior of these beams can be understood by its classical limit as skewed trajectories but still they are a very intrinsic quantum phenomenon. In fact, twisted and structured waves in general open the way to real quantum experiments. We review here our recent progresses in theory and experiments with such beams and their use in innovative measurement of magnetic fields. Fundamental aspects as the first observation of "vertical Aharonov-Bohm" effect and the new concept of optimal quantum measurement of vortex states are also briefly highlighted.

Electron vortex beams (EVB) are twisted state eigenstates of Orbital Angular Momentum (OAM) in the average propagation direction. They are the quantum superposition of a series of skewed trajectories.

Since their introduction they have been connected to magnetic measurements. One reason is that a free electron with a "twisted" wavefunction acquires naturally a magnetic dipole. For example, we recently studied the interaction of such propagating dipoles in a metallic cylinder as a new form of partially non-destructive measurement [1].

Whereas a number of techniques in electron microscopy can already probe magnetic field, such techniques show clear limitations. For example, the B component along the main propagation direction cannot be detected. However, these limitations can be overcome when EVBs are used as a probe. The "Larmor like" rotation induced by the vertical B component becomes a measureable phase for a vortex beam and can be measured by interferometry [2]. Leveraging the leadership of our group and coworkers in generating large OAM EVB [3] we have measured a new observable in electron microscopy.

Experimentally we tested this idea for an interesting case of a vertical magnetic pillar. If this magnetic pillar were approached from its side, we would have the well-known Siday-Eheremberg Aharonov-Bohm experiment. However with this experiment we have proposed an unprecedented geometry consisting of a single quantum state surrounding the magnetic flux. We are working on the interpretation of the results in terms of Berry phase and many paths theory.

We addressed also the measurement of the "in plane" component of B orthogonal to the propagation direction [4]: normally it requires the measurement of a magnetic phase by an interferometric setup. Differently in a recent study we demonstrated that the magnetic-phase measurement can be transformed in a magnetic amplitude measurement, intrinsically more efficient. This is performed by an innovative unitary transformation of the wavefunction inspired from optics. This is physically obtained by new holographic element that operates a conformal wave mapping.

On a general level a unitary transformation can be used to transform phase measurement into amplitude measurement and potentially revolutionize the measurement concept in electron microscopy.



Fig. 1

Two measurements of magnetic fields based on electron vortex beam states. (a) For a dipole along the propagation direction we used the change of the global phase. (b) For an "in plane" dipole we used a unitary basis change transforming the image in a OAM spectrum and therefore compressing the relevant information

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Highlights -Nanoscale theory modelling and computation

Introduction to Nanoscale theory modelling and computation

The research activities in the thematic area of **nanoscale theo**ry modelling and computation are aimed at developing theoretical and computational methodologies as well as their implementation in the related high performance computing software. to model and predict phenomena and experiments of systems at the nanoscale. These include first-principles approaches for molecules, small nanoparticles and materials; atomistic and coarse-grained molecular dynamics simulations for (bio)molecules; density functional theory approaches to study electronic, optical and magnetic properties of nanosystems and molecules; novel theoretical approaches to simulate the real time evolution of molecules interacting with plasmons and light; effective-mass schemes to handle complex nanostructures that are beyond the reach of first-principles tools. The impact of these methodologies ranges across various applications spanning from medicine to energy conversion, quantum optics and telecommunication, optical sensing and molecular spintronics.

Developments of advanced DFT methodologies. DFT has been extended to include the description of additional quantum states by introducing advanced functional forms. Recent theoretical developments have demonstrated that starting from standard results of first-principles simulations, it is possible to derive two estimators, namely a plasmonicity index and a "natural" metric distance of electronic correlations, to quantify the plasmonic character of optical excitations in nanostructures and the internal correlations in different materials, respectively. **Electronic, Magnetic, and Optical Properties**. Novel ab-initio modeling for the optical time resolved experiments applied to low dimensional systems, have revealed the importance of many body effect even in the low pumping regime. Ab initio ground and excited-state calculations are able to clarify the role of quantum confinement effect and of the surface orientation, in anatase nanosheets. Large scale DFT simulations have captured the microscopic mechanisms behind the magnetic coupling between magnetic molecules and substrate, and have suggested possible switching mechanisms, a key element in the realization of functional molecular magnetic devices.

Effective-mass schemes, Model Hamiltonians, and Many-Body Physics in Nanosystems. Powerful non ab-initio approaches are applied to complex nanosystems such as quantum wires, dots, carbon nanotubes, two-dimensional structures, which focus on the relevant low-energy scales to highlight complex collective quantum behavior and novel many-body insulating phases. Coarse-Grained Force Fields. Computational modeling of the membrane penetration mechanisms by peptide-aggregate could be greatly facilitated by using simplified coarse grain (CG) models. Recent strategy have been developed to build and optimize statistics based analytical CG force fields, particularly suited to account for the common interaction motives between biopolymers.

Functional magnetic molecules on conductive surfaces

The field of molecular spintronics relies on the exploitation of properties of organic molecules holding a magnetic moment posed in contact with conducting surfaces. In this study, we present a combined theoretical/experimental approach to address the behaviour of double and single phthalocyanine complexes containing either a rare earth or a 4d/5d transition metal ion adsorbed on graphene/Ni substrate. Our results demonstrate that accurate DFT-based calculations can capture the microscopic mechanisms behind the molecule-substrate magnetic coupling revealed by x-ray magnetic circular dichroism (XMCD) experiments, and suggest possible switching mechanisms, a key element in the realization of functional molecular magnetic devices.

Single ion magnets belonging to the family of bis(phthalocyaninato) lanthanide complexes (LnPc_a) are emerging as promising molecular spin (quantum) bits. In the gas phase, the magnetic moment hosted by the f orbitals of the Ln ion is flanked by a radical spin delocalized over the two Pcs. The question whether the radical spin in the Pc rings endures upon deposition on a conducting substrate, and its role in the mediation between the localized Ln spin and the outer world, is an unresolved controversial issue. We individuate a TbPc, molecule adsorbed onto a graphene (G) passivated Ni(111) surface (see Fig. 1), as an ideal system where this issue can be addressed. Low-Temperature XMCD experiments provide evidence of an antiferromagnetic interaction between the Tb and Ni magnetic moments. Density-functional theory calculations, performed in presence and absence of the graphene overlayer, strongly support the survival of the spin radical on the Pc ring in the former case. Due to an increased molecule-substrate charge transfer, the removal of graphene leads to the quenching of the spin radical, which goes hand in hand with a substantial reduction of the twist angle between the Pc planes, suggesting an exploitable functionality which intermixes the structure and magnetic properties of the molecule [1,2].

The idea of a bistable magnetic molecule is pursued even further, inspired by the works on the so-called molecular buttons [e.g., JACS 131, 3639 (2009)]: in particular, SnPc molecules have been demonstrated to retain a bistable structure (Sn ion is either above or below the Pc plane) upon adsorption on an Ag substrate. We present a proof-of-concept study to clarify whether a magnetic ion could be substituted to Sn, adding an additional degree of freedom (a magnetic moment) to the system. We find that ZrPc and HfPc molecules deposited on G/Ni(111) exhibit the Up and Down structural configurations, and are characterized by having spin-polarized orbitals (see Fig. 2) in both states, acting thus as molecular magnetic buttons [3].



Adsorption geometry of the TbPc₂ on graphene/Ni(111). The arrows represent the three different spins: the Tb, the radical on the Pcs and the Ni slab, colored yellow, green and blue, respectively. The orientation of the spins is the one attained in the ground state, as calculated by DFT.



Fig. 2

Plots of the spin densities (top panels) and of the spin-resolved LDOS (bottom panels) of a ZrPc molecule on G/Ni(III) in the structural Up and Down configurations. In the top panel, cyan (yellow) corresponds to positive (negative) spin density; in the lower panel, red and green lines and shaded gray areas represent the Pc- π , Pc- σ and Zr-d states, respectively.

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Quantifying the plasmonic character of optical excitations at the nanoscale

The microscopic description of localized surface plasmons and their identification among other excited states in nanostructures, especially where quantum effects become important, is an open issue. We introduced the concept of a plasmonicity index (i.e., a direct measure of the plasmonic character of optical excitations in nanosystems) and we provided its generalization based on rigorous theoretical derivation and numerical simulations. Our results apply on a wide range of systems, including spherical jellium nanoparticles, isolated and hybrid atomic-scale clusters, and nanostructured graphene down to its molecular limit, representing a step forward in the fundamental understanding of the nature of plasmons at the nanoscale.

Plasmons supported by metal nanostructures provide powerful tools to manipulate light at the nanoscale and are thus the basis of several potential applications, spanning from medicine to energy conversion, quantum optics and telecommunication. Textbooks loosely define plasmons as collective excitations of free-electrons in metal nanoparticles, and their current understanding is limited to a classical electrodynamics dielectric treatment of the nanoparticle. This description fails to convey a microscopic understanding of the nature of plasmons. Nanoparticles and their excitations are composed of electrons and nuclei like ordinary molecules. Therefore, it should be possible to understand their excited states, including plasmons, in terms of the same elementary electron and hole excitations used to interpret molecular excited states. However, single-particle and plasmonic excitations are inextricably mixed at the nanoscale, and the question on the way to put a plasmon label on a specific excitation is a controversial problem.

In [1], we have proposed to quantify the plasmonic nature of each transition of the optical spectrum by a number, that we called plasmonicity index (PI). The PI is directly expressed in terms of the light-induced electron density response and can be computed from standard results of first-principles simulations. The proposed expression is general and can be applied to any finite system. We have applied it to metal clusters (see Fig. 1 left), hybrid systems and molecular models of graphene nanoflakes, obtaining results conforming, a posteriori, with intuition. The PI formulation relates the plasmonicity of an excitation to its ability of enhancing locally external electromagnetic fields. In [2], a new plasmonicity index, the GPI (Generalized Plasmonicity Index), has been devised to overcome some of the limits of the initial definition. In particular, the GPI allows comparability between systems of different size (see Fig. 1 right) and can be used for classical electromagnetic calculations and for simplified quantum description such as the jellium model. Currently we are exploiting these indexes to quantify the plasmonic character of excitations in nanosystems ranging from metal clusters to molecular aggregates.



Plasmonicity Index in Ag and Si nanoclusters. (left) TDDFT absorption spectrum (black line) and Pl analysis (black diamonds and vertical lines) of Ag₂₀ (more in [1]). The inset shows the light-induced response charge density in $[Ag_{147}]^1$. (right) Comparison of GPI values computed for selected excitations of Ag and Si nanoclusters. The atomic structures of some clusters are shown as inset. The GPI identifies the excitations in Ag nanoclusters as being more plasmonic than the ones in Si nanocrystals (see [2]).

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Ferromagnetic and antiferromagnetic coupling of molecular systems driven by orbital symmetry

The moiré superstructure of graphene grown on metals can drive the assembly of molecular architectures, such as metal-phthalocyanines (MPcs), allowing for the production of artificial molecular configurations. Once FePc molecules are adsorbed on the Gr/Co surface they couple antiferromagnetically with the Co layer(s) underneath, with a magnetic remanence stable up to room temperature. At variance, CuPc molecules undergo a weaker and ferromagnetic coupling. In this study, large scale DFT simulations confirm the magnetic properties of these interfaces and highlight the role of molecular orbital symmetry as a driving force to determine the magnetic coupling.

Single atoms or molecular units with magnetic remanence at zero field have been demonstrated to enable information processing and storing at ultimate length scales. In this context, paramagnetic molecules are presented as potential building blocks in spintronics when their magnetic moments are stabilized against thermal fluctuations, e.g., by a controlled interaction with a magnetic substrate. Though room temperature (RT) operation is still elusive in standard molecular systems, magnetic remanence at RT can open the route to engineer highly spin-polarized, nanoscale current sources. The present study is motivated by the experimental need to fully control the organic spin interface and the tuning of ferromagnetic (FM) or antiferromagnetic (AFM) coupling to achieve a stable conductance.

Here, we propose to optimize the thermal stability and the magnetic remanence of molecular systems, preserving their electronic state, by exploiting interlayer exchange coupling within an advanced organic spin-interface architecture using arrays of metal phthalocyanine (MPc, M=Fe, Cu) arranged on Co layer(s) with a graphene spacer. First, the structural and electronic properties of the Gr/Co/Ir interface are characterized by comparing XPS data with ab initio simulations, showing how the XPS chemical shifts can be correlated to Gr/Co distance and registry [1]. Then the capability to mediate the super-exchange interaction by the organic ligands and the graphene spacer, preserving the magnetic state of the molecule and favouring a tuneable FM or AFM coupling with Co layer(s), is deduced by X-ray magnetic circular dichroism (XMCD) measurements and confirmed by theoretical predictions. Our results unveil the extreme sensitivity of the exchange interaction to the symmetry of the orbitals responsible for the magnetic state.

According to our simulations, as reported in Fig. 2, for FePc, the spin of the central ion is oriented opposite to the one of N and C, and antiferromagnetically coupled with the underlying Co spin moment. In the case of CuPc, the spin imbalance is located at the central ion and on the surrounding N atoms, and coupled ferromagnetically with the Co spin moment. A detailed analysis of Lowdin charges can also be used to further discriminate the symmetry of the molecular orbitals involved in the magnetic coupling. The above picture is very robust against the use of different exchange and correlation functionals (LDA, PBE, PBE+U, discussed in the Supplemental Material), and is in excellent agreement with the experimental data, fully supporting the picture where

the magnetic coupling of MPc with Gr/Co/Ir is mainly driven by the symmetry of the involved molecular orbitals.



Fig. 1

Top left panel: a cartoon of the corrugated Graphene as given by the egg-box model. Bottom left panels: CIs core-level shifts (CLS) computed for the two non-equivalent C atoms of Gr/Co(0001) in top-fcc registry (C atoms at fcc-hollow and on-top sites), with increasing graphene-Co distance and represented as Lorentzian functions with a width of 0.1 eV. The average of the CLS computed for GR/top-fcc at 2.05 Ang distance was used as reference, here set to zero. Aside: top view of the studied fcc-top Gr/Co(0001) geometry with grey representing C and blue Co atoms. The top Co layer is represented in lighter blue. The 1x1 unit cell is reported. Circle and triangle symbols refer to fcc and top adsorption sites, respectively. Diamond symbols correspond to the hcp site. Right panels: (a) Core-hole shift dependence with C-Co distance computed for Gr/Co. The red line gives the average of the values computed for the two non-equivalent C sites of four different registries of commensurate Gr/Co, shown by the symbols in different colours. (b) Height distribution for corrugated Gr/Co as given by the egg-box model. (c) XPS spectra computed as a sum of Lorentzian functions centred in the core-hole energies given in the left panel. (d) Experimental CIs XPS spectra.

Fig. 2

XMCD from Fe and Cu L2,3 absorption edges (a,d), hysteresis loops of FePc (b) and CuPc (e) on Gr/IML Co. The change in the sign of the XMCD (a,d) and of the field-dependent magnetization (b,e) indicate an AFM for FePc/Gr/Co and a FM for CuPc/Gr/Co. Spin-density isosurface plots for FePc and CuPc on Gr/Co/ Ir (side and top view with hidden substrate), computed at the DFT-PBE+U level, U=4 eV (c,f). The geometry optimization includes PBE-D2 van der Waals corrections. Green (red) isosurfaces correspond to the up (down) spin density.



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Toward multiscale simulations of peptide bilayer interactions

As highlighted by increasing scientific evidence, the crossing of biological membrane by cell penetrating peptides (CPPs) is governed by their self-association. We report a combined experimental and computational study showing that Tat_{11} , a CPP, is able to form dimers despite its sizeable positive charge. By extensive MD simulations, we unraveled the structural motives of Tat_{11} self-association, providing the basis to understand the membrane penetration mechanisms. Computational modeling of the peptide-aggregate interaction with the membrane can be greatly facilitated by using simplified coarse grain (CG) models. Here we also describe a strategy to build and optimize statistics based analytical CG force fields, particularly suited to account for the common interaction motives between biopolymers.

Molecular dynamics (MD) simulations of aggregation phenomena become particularly challenging when dealing with intrinsically disordered proteins, such as the highly charged Tat, peptide. The complexity of aggregation per se is compounded with the requirement of exhaustively sampling the numerous peptide conformations. Notwithstanding this complexity, the topic is of broad interest given its recurrence in several biological phenomena. One example is the mechanism of Tat, internalization (through the biological membrane), being concentration dependent in a way that mirrors the aggregation state of the peptide in solution. Light scattering and NMR measurements of the diffusion coefficient (Fig. 1a) provide a picture suggesting the presence of a dimeric aggregate. These observations prompted us to investigate putative structure of Tat, dimer by MD all-atom simulations. Starting configurations were obtained by maximizing the inter-peptide contacts by metadynamics, and unrestrained MD simulations at the us timescale. The dimer structures were provided to be highly flexible with the inter-peptide interactions taking place mostly between the C-termini. In this arrangement the negatively charged carboxylic groups (COO⁻) engaged in salt bridges with the several charged side chains (see Fig. 1b). A notable feature was the presence of stacking between two or more Arg guanidinium groups close to the C-termini. Albeit keeping two positively charged groups in close contact, this motif optimized the geometry for the interaction with COO⁻ (Fig. 1b). The question whether this stacking is functional to the peptide interaction with the membrane will be the topic of further studies.

In spite of their increasing use, Coarse Grained (CG) models for biopolymers are still far from reaching the level of standard and validation currently available for all-atom models. This depends in part on the fact that the parameterization strategies are various and most often adjusted on the specific cases. We made an effort to design a general strategy to aid building and optimization of statistics based analytical force fields which we implemented in the software AsParaGS (Assisted Parameterization platform for Coarse Grained models, http://www.muscade-lab.it/project/asparags). The method rely on the exploration of the parameters space of the analytical interaction potential by combining different algorithms (i.e., relative entropy driven

stochastic exploration and iterative Boltzmann inversion) and searching for optimal parameters set with respect to given score function, e.g., depending on the distance of simulation and experimental distribution function of structural variables.





Fig. 1

Panel a): Diffusion coefficients obtained by NMR DOSY experiments for increasing peptide concentrations. Monomer and dimer diffusion coefficients (D_{mon} and D_{dim} , respectively) with dimerization constant (K_{dim}) are obtained by fitting. Panel b): Tat_n inter and intra peptide contact map averaged during the simulation, and dimer representative structure. Single letter amino acids are indicated for each monomer. The inset shows the Arg-Arg stacking motif with salt bridges between C-termini and Arg side chains.

Fig. 2

Illustration of the AsParaGS method on a test case (helical polypeptide). On the left: the parameters space is explored until the helical-stabilizing parameterization is reached, as shown in the Ramachandran Map. On the right: the methods allow revealing correlations between parameters: if two terms in the force filed are correlated (e.g., the bond angle and 1-3 interaction term), areas with similarly high scores appear in the parameters space (blue color), indicating that any combination of these two terms lying on the correlation line will give similarly good force fields.

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Advancing the theory of density functionals to simulate novel materials

Predicting properties of materials at the nanoscale is an endeavor that leads to enormous practical benefits. The task requires translating the laws of quantum mechanics into tractable computations. Density functional theory (DFT) provides an ideal framework where theory and applications meet. The ever increasing demand of new materials and of more versatile predictions prompt us to design new ways of exploiting DFT methods and of extending them to novel quantum states. Here we describe our most recent contributions.

Properties of materials emerge from the way electrons are shared among atoms. The underlying network of interactions makes the simulations of materials a formidably difficult task. DFT comes to our rescue by mapping the real problem into a virtual problem of non-interacting electrons keeping track of the intricate correlations by functionals of the particle density which can be usefully approximated and thus practically applied.

Searching for novel materials with special properties, it provides us with useful hints to quantify how different the internal correlations of a system are from those of others. For this purpose – by exploiting DFT functionals [1] – we introduce a physically appealing and practical way of measuring distances between the correlations which are induced by the antisymmetry requirement for the many-electron wave function. In Fig. 1 we show an application of the newly defined distance to atoms.

Non-collinear magnetism, spintronics, orbitronics, and topological states are pivotal to many anticipated quantum technologies. An improved DFT approach to treat these systems should use as basic variables the current, the spin-current, and the spin density besides the particle density. But finding simple and effective approximations for such an extended DFT has been a long-standing challenge. In [2], we propose a way out of this impasse by introducing a set of minimal substitutions to generate new approximations from established ones by satisfying the most characterizing exact property of the extended functionals.

Relevant properties of materials can also involve excited states, e.g., in photovoltaics. Ensemble DFT is a generalization of DFT which was intended to simplify the calculation of excited energy levels. Its application, however, has been hampered by formal difficulties of breaking its complicated functionals into more elementary components. In [3], we introduce a long-sought unproblematic ensemble density functional to capture first-order electron-electron interaction effects which is amenable to both applications and further approximations.



The distance, D_x , introduced in [1] is here computed between atoms with atomic numbers Z and Z-1 and is plotted against Z for the s and p blocks of the periodic table. The curve peaks when considering the last atom of one row and the first of the next. The expected periodicity is well reflected in the behaviors of D_x .

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Ultrafast Response of Single-Layer MoS₂: insights from first-principle simulations

Transition metal dichalcogenides (TMDs) are emerging as promising two-dimensional (2D) semiconductors for optoelectronic and flexible devices. Femtosecond spectroscopy with pump pulse tunability and broadband probing shows that, irrespective of excitation photon energy, the transient absorption spectrum of single-layer MOS_2 is characterized by the simultaneous bleaching of all excitonic transitions and corresponding red-shifted photoinduced absorption bands. Novel ab initio modeling of the ultrafast optical response reveals that the bandgap renormalization due to photoexcited carriers is primarily responsible for the observed features.

Molybdenum disulfide (MoS_2) and related TMDs are acquiring an ever increasing attention due to the potential technological impact of their electronic and optical properties, e.g., sizable gaps in the visible-NIR range and the peculiar indirect-to-direct bandgap crossover when reaching the monolayer thickness. A wealth of studies has already appeared for their exploitation in novel optoelectronic and flexible devices, especially in combination with other atomically thin materials. However, a more fundamental understanding of their photophysics – of pivotal importance for the device optimization – is still lacking. Femtosecond transient absorption spectroscopy with tunable pump pulses and broadband probing is used to monitor the relaxation dynamics in single-layer MoS_2 over the entire visible range. Irrespective of the excitation energy, the transient absorption spectrum shows three prominent features, each consisting of a bleaching of the main excitonic transition and a red-shifted photoinduced absorption.

We apply a novel ab initio approach that combine non-equilibrium Green's functions with density-functional theory methods for the simulation of the carrier dynamics upon photoexcitation [1]. Our findings, fully accounting for electron-electron and electron-hole interactions, reveal that Pauli blocking cannot explain, alone, the simultaneous bleaching of the three excitonic transitions and the corresponding photoinduced absorption. Instead, a transient band gap renormalization (BGR), caused by the presence of photo-excited carriers, is found as the key mechanism governing the carrier dynamics after photo-excitation. Our results demonstrate the strong impact of many-body effects in the transient optical response of TMDs even in the low-excitation-density regime.



a-b. Linear and transient absorbance of 1L-MoS₂. The pump-probe experiment shown in panel b is performed by pumping in resonance with Å (ω_{pump} = 1.88 eV, red arrow) and B (ω_{pump} = 2.06 eV, green arrow), and out of resonance with C (ω_{pump} = 3.10 eV, blue arrow); the probe pulse covers the entire visible range (1.6–3.2 eV). c. Calculated transient absorption spectra of 1L-MoS₂ for three pump photon energies, i.e., 1.88 eV, 2.01 eV, and 2.83 eV, including both Pauli blocking and BGR. d. Electronic band structure (black) of 1L-MoS₂ at the K-point and its optical excitations (red) in absence (left) and in presence (right) of pump pulse absorption. The overall shift of the excitonic absorption of the exciton binding energy, due to the presence of photoexcited carriers, i.e., $\delta = \Delta Eg - \Delta Eb$.

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 Photo-Induced Bandgap Renormalization Governs the Ultrafast Response of Single-Layer MoS₂. E. A. A. Pogna, M. Marsili, D. De Fazio, S. Dal Conte, C. Manzoni, D. Sangalli, D. Yoon, A. Lombardo, A. C. Ferrari, A. Marini, G. Cerullo, and D. Prezzi. ACS NANO 10, 1182 (2016). It has long been anticipated theoretically that semiconductors with small band gaps may form a correlated excitonic insulator phase, but it has been difficult to find material realisations. Here, on the basis of complementary first-principles calculations, the authors predict that zero-gap armchair carbon nanotubes could be excitonic insulators.

Fifty years ago Walter Kohn speculated that gray tin -a zero-gap semiconductorcould be unstable against the tendency of mutually attracting electrons and holes to form bound pairs, the excitons. Being neutral bosonic-like particles, the excitons would spontaneously occupy the same macroscopic wave function, resulting in a reconstructed insulating ground state with a broken symmetry inherited from the exciton character. This excitonic insulator (EI) would share intriguing similarities with the Bardeen-Cooper-Schrieffer (BCS) superconductor ground state, the excitons-akin to Cooper pairs-forming only below a critical temperature and collectively enforcing a quasiparticle gap. Overall, the observation of the EI remains elusive.

Carbon nanotubes, being rolled cylinders of graphene whose low-energy electrons are massless particles, exhibit strong excitonic effects, due to ineffective dielectric screening and enhanced interactions resulting from one dimensionality [1]. As single tubes can be suspended to suppress the effects of disorder and screening by the nearby substrate or gates, the field lines of Coulomb attraction between electron and hole mainly lie unscreened in the vacuum (Fig. 1). Consequently, the interaction is truly long ranged and in principle -even for zero gap- able of binding electron-hole pairs close to the Dirac point in momentum space (Fig. 2). If the binding energy is finite, then the ground state is unstable against the spontaneous generation of excitons having negative excitation energy, $\varepsilon_u < 0$. This is the analog of the Cooper instability that heralds the transition to the superconducting state-the excitons replacing the Cooper pairs.

Here we focus on the armchair family of zero-gap carbon nanotubes, because symmetry prevents their gap from opening as an effect of curvature or bending [2]. We show that armchair tubes are predicted to be EIs by first-principles calculations. By using the GW and Bethe-Salpeter schemes we find that bound excitons exist in the (3,3) tube with finite negative excitation energies. By performing unbiased quantum Monte Carlo simulations we prove that the reconstructed ground state is the EI, its signature being the broken symmetry between inequivalent carbon sublattices-reminescent of the exciton polarization. Finally, to investigate the trend with the size of the system, which is not yet in reach of first-principles calculations, we introduce an effective-mass model, which shows that both EI gap and critical temperature fall in the meV range and scale with the inverse of the tube radius. Our findings are in contrast with the widespread belief that electrons in undoped armchair tubes form a Mott insulator-a strongly correlated Luttinger liquid.



Sketch of a suspended armchair carbon nanotube. The field lines of the Coulomb force between electron and hole lie mainly in the vacuum, hence screening is heavily suppressed.



Fig. 2.

Excitonic instability of an armchair carbon nanotube. The scheme represents the excitation energy ε_u of an electron-hole (e-h) pair relative to the noninteracting ground state, a zero-gap semiconductor. In the absence of interaction, the excitation energy ε_u of an e-h pair is positive. The long-range interaction may bind e-h pairs close to the Dirac point in momentum space. If an exciton forms, then its excitation energy ε_u is negative. This instability leads to the reconstruction of the ground state into an excitonic insulator.

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Role of Quantum-Confinement in Anatase Nanosheets

Among semiconducting oxides, TiO_2 is the most widely used for energy and environmental oriented applications. In this regard, nanostructured TiO_2 -based materials are largely investigated due to the enhancement of the surface area and to the observed improvement of photochemical and photo-physical activity with respect to the bulk phase. Here, by means of ab initio ground and excited-state calculations, we reveal, in an unambiguous way, the role of quantum confinement effect and of the surface orientation, on the electronic and optical properties of anatase nanosheets (NSs). The presence of bound excitons extremely localized along the (001) direction, whose existence has been recently proven also in anatase bulk, explains the different optical behavior found for the two orientations (001) and (101) when the NS thickness increases

Despite most of the applications of anatase nanostructures rely on photoexcited charge processes, yet profound theoretical understanding of fundamental related properties is lacking. We studied by means of post-DFT excited-state (namely GW ad Bethe– Salpeter Equation (BSE)) calculations the impact of quantum-confinement (QC) effect on the electronic and optical properties of anatase nanostructures focusing on (001) and (101) anatase NSs of increasing thickness [1]. Our results demonstrate the presence of a mismatch between electronic and optical gap, with the latter mainly associated with the presence of strongly bound bidimensional excitons, confirming the results recently reported for the bulk anatase.

Figure 1a and 1b show the optical spectra of the (001) and (101) anatase NSs compared to the corresponding optical spectrum of anatase bulk where we note that increasing the sheet thickness, the position of the first optical peak rapidly recovers the bulk-like position for the (001) orientation while a larger QC effect for the (101) case is clearly visible. In Fig. 1c, we report the value of the direct and indirect QP electronic gaps together with the energy of the first bright exciton as a function of the (001) sheet thickness: it is clear that the electronic and optical gaps have a different behavior decreasing the thickness of the nanosheet. Indeed, the electronic QP direct and indirect gaps remain larger than the corresponding bulk value for the considered thicknesses while the optical (excitonic) direct gaps converge more rapidly to the optical direct gap of the bulk as soon as the bulk-like excitonic wave function is contained in the NS thickness, which is at $d \sim 2$ nm.

The top and bottom panels of Fig. 2 report the exciton spatial distribution for the (001) and (101)-NS (d = 1.8 nm), showing the same high degree of spatial localization, along the c-axis, observed in bulk. In both cases, the probability of finding the photoexcited electron in or near the (001) crystallographic plane where the hole has been created is large, while it rapidly decreases along the [001] direction. A bulk-like behavior of the optical spectrum is rapidly recovered in the (001)-oriented NSs with a threshold thickness value (\sim 2 nm), while a larger QC effect is visible in the (101) NSs

of comparable thickness, due to the fact that, in this case the excitonic wave function extends up to the two surfaces, remaining confined. We suggest that the almost 2D nature of these excitons can be related to the improved photoconversion efficiency observed when a high percentage of (001) facet is present in anatase nanocrystals.



Fig. 1

Top: Optical spectra calculated within the GW/BSE approach of bulk, anatase (001) (a) and (101) (b) for light-polarized \perp c-axis. First dark (D) and bright (B) excitons are also indicated. The (101) Ns presents larger QC effect. Bottom: Direct (squares) and indirect (diamonds) electronic (QP) gaps; first bright (circles) excitons (BSE) as a function of nanosheet thickness. Scaling law fits $\simeq 1/d^{\alpha}$, where d is the nanosheet thickness, are similarly reported. The red (blue) and yellow solid lines represent the QP direct (indirect) and optical direct gap in bulk.

Fig. 2

Top (left) and side (right) views of the spatial distribution of the electron-hole wave function for the first exciton for the thicker (001) (top panel) and (101) (bottom panel) sheets. The light-blue ball represents the hole position. A bulk behaviour is recovered for (001) sheet of thickness of about 2nm, the exciton wave function of (101) Ns of similar thickness extends up to the two surfaces.

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Projects and grants

Cnr Nano research activity is mainly supported by funding obtained through competitive calls at different levels, from international to local. Projects running in 2016–2017 are listed below with following details: project name, call details, project ID, coordinator, Cnr Nano principal investigator (if different), dates, website (if available). A short abstract is given for European-funded projects. For further information, contact the project's Cnr Nano principal investigator. **COMANCHE**. Coherent manipulation and control of heat in solid-state nanostructures: the era of coherent caloritronics. FP7-IDEAS-ERC; ID 615187. Cnr Nano Pisa (F. Giazotto). 2014-2019.

Abstract. Electronic nanodevices have demonstrated to be versatile and effective tools for the investigation of exotic quantum phenomena under controlled and adjustable conditions. Yet, these have allowed giving access to the manipulation of charge flow with unprecedented precision. On the other hand, the wisdom dealing with control, measurements, storage, and conversion of heat in nanoscale devices, the so-called "caloritronics" (from the Latin word "calor", i.e., heat), despite a number of recent advances is still at its infancy. Although coherence often plays a crucial role in determining the functionalities of nanoelectronic devices very little is known of its role in caloritronics. In such a context, coherent control of heat seems at present still very far from reach, and devising methods to phase-coherently manipulate the thermal current would represent a crucial breakthrough which could open the door to unprecedented possibilities in several fields of science. Here we propose an original approach to set the experimental ground for the investigation and implementation of a new branch of science, the "coherent caloritronics".



FLAGSHIP GRAPHENE. Graphene-Based Revolutions in ICT and Beyond Graphene FP7-ICT ICT-2013.9.9; ID 604391. Chalmers Tekniska Hoegskola AB, SE (J. Kinaret); Cnr Nano Pisa (V. Tozzini and M. S. Vitiello). 2013-2016. www.grapheneflagship.eu

Abstract. This Flagship project "Graphene-Based Revolutions" aims to take graphene and related layered materials from a state of raw potential to applications in different fields such as flexible, wearable and transparent electronics, to new energy applications. During 2013-2018, Cnr Nano has been involved in two workpackages, "Energy Applications" and "Optoelectronics". Within the energy application field Cnr Nano participated in the fundamental study of the possibility of using graphene as hydrogen storage medium, using a multi-disciplinary approach involving the manipulation and analysis of hydrogenated epitaxial graphene and multi-scale computer simulations. Within the Optoelectronics workpackage Cnr Nano is involved in the development of high speed photodetectors operating at Terahertz frequencies, resonant plasma wave photodetectors based on graphene, and related 2D materials and saturable absorbers exploiting graphene.

GRAFLEX. Graphene curvature, flexibility and reactivity control by means of external fields; theory and computer simulations. H2020-MSCA-IF-2014; ID 657070. Cnr Nano Pisa (V. Tozzini). 2015-2017.

Abstract. Graphene has a unique combination of thermal, mechanical, and electronic properties, particularly its flexibility, which makes it especially interesting for applications in several high-tech applications. Among these, the interplay between electronic and mechanical properties has been little investigated, and this prevents their full exploitation. The aim of GRAFLEX is to investigate the process of curvature control by means of external electric and electromagnetic fields (EM), and the consequent curvature-dependent interaction with hydrogen (or other substances), for energy and flexible electronics applications. The tools used are the state-of-the-art density functional (DF), DF perturbation, and trajectory based, time-dependent DF theories, in combination with ab initio investigation of the kinetics of the underlying reactions and calculation of converse flexoelectricity response to the strain gradient in curved graphene.



MaX. Materials design at the exascale. H2020-EINFRA-2015-1; ID 676598. Cnr Nano Modena (E. Molinari). 2015-2018. www. max-centre.eu

Abstract. Materials are crucial to scientific and technological advances and industrial competitiveness, and to tackle key societal challenges - from energy and environment to health care, information and communications, manufacturing, safety and transportation. The current accuracy and predictive power of materials' simulations allow a paradigm shift for computational design and discovery, in which massive computing efforts can be launched to identify novel materials with improved properties and performance; behaviour of ever-increasing complexity can be addressed; sharing of data and work-flows accelerates synergies and empowers the science of big-data; and services can be provided in the form of data, codes, expertise, turnkey solutions, and a liquid market of computational resources. Europe has the human resources, track record and infrastructure to be worldwide leader in this field, and we want to create a CoE in materials' modelling, simulations, and design to endow our researchers and innovators with powerful new instruments to address the key scientific, industrial and societal challenges that require novel materials.



MIR-BOSE. Mid- and far-IR optoelectronic devices based on Bose-Einstein condensation. H2020-FETOPEN-1-2016-2017; ID 737017. Université Paris Sud (R. Colombelli); Cnr Nano Pisa (M. S. Vitiello). 2017-2020. www.mir-bose.eu

Abstract. The MIR-BOSE project will demonstrate disruptive optoelectronic devices operating in the strong coupling regime between light and matter. In particular, we will demonstrate the followings: the first bosonic lasers operating in the mid-IR and THz frequency ranges of the electromagnetic spectrum. Second, a new

concept of inverse-Q-switching leading to the generation of high power pulses in the mid-IR ranges, overcoming severe bottlenecks in current technology. Finally, non-classical/quantum light sources and devices based on ultra-fast modulation of the light-matter interaction, generating squeezed states of light in the mid-IR/THz spectral range for quantum optics applications. These new sources will have a major impact on a wide range of technologies and applications in the mid-IR and THz frequency ranges, being advantageous compared to current commercial solutions.

MODENADYNA. MODeling Electron Non-Adiabatic DYNAmics. FP7-PEOPLE-2013-IIF; ID 623413. Cnr Nano Modena (C. A. Rozzi). 2015-2017.

Abstract. The aim of MODENADYNA is to push Time-Dependent Density Functional Theory (TDDFT) beyond the present 'state of the art' by implementing a novel computational scheme to MODel Electron Non-Adiabatic DYNAmics due to electron-electron scattering processes. This goal matches the needs of: (i) going beyond the simplest adiabatic approximation – commonly adopted in the description of ultrafast phenomena at the nanoscale; and (ii) dealing with the actual spatial inhomogeneities of many-electron systems at non-adiabatic level.



MOLARNET. Molecular Architectures for QCA-inspired Boolean Networks. FP7-ICT-2011-8; ID 318516. Cnr Nano (R. Rinaldi). 2012-2016. www.nano.cnr.it/MOLARNET/joomla/public_htm

Abstract. Achievement of ever higher levels of integration in microelectronics will eventually require a radical shift from the field-effect transistor (FET) based paradigm to a revolutionary approach to computing. Quantum-dot Cellular Automata (QCA) is an alternative vision to binary computing since no current flow is required to encode binary information, and has been considered one of the most promising post-Moore alternatives. Implementation and miniaturization of QCA at the molecular level offer important advantages, including the perspective of room temperature operation, an essential step for industrial exploitation. However, the small sizes of the building blocks lead also to severe challenges when addressing the single elementary units. The present project specifically addresses the basic requirements to implement molecular QCA-inspired Networks.

MOQUAS Melecular Quantum Spintronics FP7-ICT-2013-10 **MOQUAS**. Molecular Quantum Spintronics. FP7-ICT-2013-10; ID 610449. Cnr Nano Modena (M. Affronte). 2013-2016. www. moquas.eu

Abstract. MoQuaS aims at developing devices and protocols to read out and process quantum information using individual molecular spins embedded in electronic circuits. To this end, prototypical hybrid nano-devices addressing single molecular spins will be designed and reliable methods for their realization will be developed. Core of such nano-architectures are magnetic molecules, specifically functionalized

to graft electrodes, and exploited as spin (qu)bits. MoQuaS designed and realized the necessary platform for the read out and the manipulation of the electron and nuclear states of single molecules.



NANOREG. A common European approach to the regulatory testing of nanomaterials. FP7-NMP-2012-LARGE-6; ID 310584. Ministerie van Infrastructuur en Milieu-Dip. SCTM, NL (T. van Teunenbroek); Cnr Nano Pisa (G. M. Ratto). 2013-2016. www. nanoreg.eu

Abstract. The innovative and economic potential of Manufactured Nano Materials (MNMs) is threatened by a limited understanding of the related EHS (Environmental Health and Safety) issues. While toxicity data is continuously becoming available, the relevance to regulators is often unclear or unproven. The shrinking time to market of new MNM drives the need for urgent action by regulators. NANOREG has been the first FP7 project to deliver the answers needed by regulators and legislators on EHS by linking them to a scientific evaluation of data and test methods.



NANO-JETS. Next-generation polymer nanofibers: from electrified jets to hybrid optoelectronics. FP7-IDEAS-ERC; ID 306357. Cnr Nano (D. Pisignano). 2013-2018. www.nanojets.eu

Abstract. This project ultimately targets the application of polymer nanofibers in new cavity-free lasers. To this aim, it wants to tackle the still unsolved problems of the process of electrospinning in terms of product control by the parameters affecting the dynamics of electrified jets. The electrospinning is based on the uniaxial elongation of polymeric jets with sufficient molecular entanglements, in presence of an intense electric field. It is a unique approach to produce nanofibers with high throughput. This project aims at elucidating and engineering the still unclear working principles of electrospinning by solutions incorporating active materials, with a tight synergy among modelling, fast-imaging characterization of electrified jets, and process engineering. Once optimized, nanofibers will offer an effective, well-controllable and cheap material for building new, cavity-free laser systems.

M PHENOMEN

PHENOMEN. All-Photonic Circuits enabled by opto-mechanics. H2020-FETOPEN-2014-2015-RIA; ID 713450. ICN2, ES (C. Sotomayor Torres); Cnr Nano Pisa (A. Pitanti). 2016-2019. www. phenomen-project.eu

Abstract. Phenomen aims at building a phononic chip platform, where coherent vibrations above 1 GHz can be generated, routed and detected via optomechanical devices operating at room temperature. Adding novel functionalities in phonon processing such as switching and modulation, the technology developed in Phenomen will enable the coupling of different physical (quantum) systems towards the realization of the ultimate hybrid platform, where photons, electrons, and phonons can be interchangeably used for information manipulation and control.

PHOSFUN. Phosphorene functionalization: a new platform for advanced multifunctional materials. ERC-2014-ADG; ID 670173. Cnr Iccom (M. Peruzzini) and Cnr Nano Pisa (S. Heun). 2015-2019.

Abstract. 2D materials have attracted a great deal of interest due to their variety of applications. Since its discovery in 2004, graphene has monopolized the attention given the unparalleled combination of outperforming structural and functional properties which pave the way for a plethora of different applications. Nonetheless its applicability in micro- and nanoelectronic has been later demonstrated to be strongly limited due to its inherent lack of a band gap. This limitation could be overcome using phosphorene, a recently discovered 2D sheet formed by phosphorus atoms prepared by exfoliation of black phosphorus and endowed with a natural band gap. The PHOSFUN proposal focuses on the unexplored chemical reactivity of phosphorene and gathers together chemists mastering the chemistry of phosphorus with physicists expert in advanced nanostructured systems. First, we aim to set-up a scalable and reproducible synthesis of mono and multilayer phosphorene.

Q-SORT Q-SORT. Quantum sorter. H2020-FETOPEN-1-2016-2017; ID 766970. Cnr Nano Modena (V. Grillo). 2017-2021. www.qsort.eu

Abstract. Q-SORT introduces a revolutionary concept whereby the transmission electron microscope (TEM) is employed as a so-called Quantum Sorter, i.e., a device that can pick out and display detailed information about electron quantum states. This in turn provides researchers with precious new information about the sample being examined. The project -which includes applications in physics, biology, and biochemistry- is expected to have a wide-ranging impact due to the ubiquitous adoption of TEM and STEM across many disciplines. Q-SORT also has foundational value in physics as it fosters its own kind of sparse-sensing approach to TEM, advancing the field in the direction of quantum measurement.



REDOX. Reducible oxide chemistry, structure and functions. COST ACTION CM1104. Universität Osnabrück, DE (M. Reichling); Cnr Nano Modena (P. Luches). 2012–2016. www.cost-redox.nano.cnr.it

Abstract. Redox is a European project that explores and develops reducible oxides for applications such as chemical catalysis, sustainable energy conversion and novel electronic devices. Objective driven experimental and theoretical research devoted to exploring the origins and details of reducibility in oxides, creating novel routes for

the growth and synthesis of nanostructured reducible oxide systems, exploiting and tailoring reducibility in oxide systems to yield specific functionalities and exploring novel applications and visionary concepts for the future use of reducible oxide materials.

SOULMAN. Sound–Light Manipulation in the Terahertz. FP7-IDEAS-ERC; ID 321122. Università di Pisa, IT and Cnr Nano Pisa (A. Tredicucci). 2013-2018.

Abstract. The interaction of electromagnetic radiation with the mechanical vibrations of solids affects and determines many different physical phenomena. At the microscopic level, scattering of light with phonon excitations is a well-known process exploited in semiconductor devices like Raman amplifiers and acousto-optic modulators. At the macroscopic scale, the interaction is mediated by the radiation pressure and is raising considerable interest as a way to excite and control mechanical oscillators, allowing, for instance, the refrigeration of a macroscopic object near the quantum limit. This rich physics has been mostly developed in the visible or near-infrared spectral ranges. SouLMan aims at establishing the new field of THz opto-mechanics based on quantum cascade technology, at investigating the phenomena and concepts that become available in this spectral range and in optically active systems, and at using this knowledge to implement innovative device functionalities and applications.

SPRINT. Ultra-short pulse laser resonators in the Terahertz. H2020-ERC-CoG-2015. Cnr Nano Pisa (M. S. Vitiello). 2016-2021.

Abstract. Ultra-short light pulses with large instantaneous intensities can probe light-matter interaction phenomena, capture snapshots of molecular dynamics and drive high-speed communications. In a semiconductor laser, mode-locking is the primary way to generate ultrafast signals. Despite the intriguing perspectives, operation at Terahertz (THz) frequencies is facing fundamental limitations: engineering "ultrafast" THz semiconductor lasers from scratch or finding an integrated technology to shorten THz light pulses are currently two demanding routes. SPRINT aims to innovatively combine the ground-breaking quantum cascade laser (QCL) technology with graphene, to develop a new generation of passive mode-locked THz photonic laser resonators, combined with unexplored electronic nanodetectors for ultrafast THz sensing and imaging.

SuperMag. Cooperation between Superconductivity and Magnetism in Mesoscopic Systems: towards Majorana States. H2020-MSCA-IF-2014; ID 660532. Cnr Nano Pisa (F. Giazotto). 2015-2017.

Abstract. A major challenge in contemporary physics is to understand and control unconventional states of matter, such as topological superconductors and Majorana

fermions (MFs). Once harnessed, this physics offers bright prospects for low-power superconducting digital electronics and fault-tolerant quantum computation. Recent proposals showed that ordered chains of magnetic impurities, in proximity of a superconductor, can hold a MFs. Specifically, the project combined two novel technologies: (i) the superconducting quantum interference proximity transistor (SQUIPT) and (ii) the molecular spin doping.



TAME-Plasmons. Theoretical chemistry Approach to tiME resolved molecular Plasmonics.H2020-ERC-CoG-2015; ID 681285. Università di Padova, IT and Cnr Nano Modena (S. Corni). 2016-2021. www.tame-plasmons.eu

Abstract. Ultrafast spectroscopy is a powerful tool able to disclose the atomistic real-time motion picture of the basic chemical events behind technology and life, such as catalytic reactions or photosynthetic light harvesting. Nowadays, by cleverly harnessing the interaction of the studied molecules with plasmons (collective electron excitations supported, e.g., by metal nanoparticles) it is becoming possible to focus these investigations on specific nanoscopic regions, such as a portion of a catalytic surface or of a photosynthetic membrane. The goal of TAME-Plasmons is to develop a theoretical chemistry approach to directly simulate the real-time evolution of molecules interacting with plasmons and light.



TherMiQ. Thermodynamics of Mesoscopic Quantum Systems. FP7-ICT-2013-C; ID 618074. The Queen's University of Belfast, IE (M. Paternostro); Cnr Nano Pisa (G. M. Palma). 2014-2016. www.thermiq2.eu

Abstract. TherMiQ brings together thermodynamics and the physics of open quantum mesoscopic systems through an innovative research project that combines thorough theoretical investigations and cutting-edge experimental demonstrations. Its founding idea of is to exploit quantum mesoscopic devices to address three targeted goals: 1. The unambiguous definitions of genuinely quantum thermodynamical quantities; 2. The construction of mesoscopic thermal engines and the arrangement of heat/mass/entropy transport mechanisms working at the quantum level; 3. The test of the foundations of quantum mechanics through thermodynamical concepts.



ULTRAQCL. Ultrashort Pulse Generation from Terahertz Quantum Cascade Lasers. UE H2020-FETOPEN-2014-2015-RIA; ID 665158. CNRS-LPA, FR (S. Dhillon); Cnr Nano Pisa (M. S. Vitiello). 2015-2018. www.ultraqcl.eu

Abstract. The generation of ultrafast and intense light pulses is an underpinning technology across the electromagnetic spectrum enabling the study of fundamental

light-matter interactions, as well as industrial exploitation in a plethora of applications across the physical, chemical and biological sciences. However, in the terahertz (THz) frequency range, with its proven applications in imaging, metrology and non-destructive testing, a semiconductor based technology platform for intense and short pulse generation has yet to be realised. Ultrafast excitation of photoconductive switches or nonlinear crystals offer only low powers, low frequency modulation or broadband emission with little control of the spectral bandwidth. In the ULTRAQCL project we will breakthrough this technological gap, using THz quantum cascade lasers (QCLs) as a foundational semiconductor device for generating intense and short THz pulses.

Understanding and Controlling Nano and Mesoscale Friction. MPNS COST ACTION MP1303. Università degli Studi di Milano, IT (N. Manini); Cnr Nano Modena (G. Paolicelli). 2013-2017. www.nanofriction.org

Abstract. Recent years have seen widespread efforts to understand the mechanisms of friction and tribology in micrometric structures (mesoscale) down to the realm of atoms and molecules (nanoscale), with the ultimate goal of controlling friction, adhesion and wear by design. This research has generated an interdisciplinary scientific area, nanotribology, with great potential impact on technology and everyday life. Applications include safety, economy, life quality, energy, and material saving, toward a sustainable development. Europe has a strong scientific nanotribology community spreading over physics, materials science, chemistry, earth and life sciences. So far, this community lacks a chance to interact closely enough: it is in urgent need of better networking, to favor collaboration among groups and exchange of complementary expertise.

xPRINT. 4-Dimensional printing for adaptive optoelectronic components. ERC-CoG-2015; ID 682157. Cnr Nano Pisa (A. Camposeo). 2016-2021.

Abstract. Additive manufacturing of three-dimensional objects relies on depositing or curing materials in a layer-by-layer fashion, starting from computer assisted design. These technologies have rapidly evolved from laboratory research to commercially available desktop systems, with costs decreasing continuously. Notwithstanding such astonishing progress, the potentialities of three-dimensional printing are still poorly exploited in terms of both materials and process resolution. This project will shed new light on the fundamental aspects of three-dimensional polymerization, thus establishing new process design rules and predictive tools for printing resolution. It will also specifically engineer additive manufacturing for printing materials embedding active compounds, thus leading to four-dimensional objects, namely structures that have three-dimensional features and time-changing physical properties at the same time.
Assessing protein system dynamics and thermodynamics: a novel NMR approach at single residue resolution. MIUR PRIN 2012. Università degli Studi di Udine (G. Esposito); Cnr Nano Modena (S. Corni). 2014-2017.

Caloritronica coerente in sistemi mesoscopici a superconduttore. MIUR FIRB FR 2013. Cnr Nano Pisa (C. Oriol Altimiras Martin). 2014-2017.

Dispositivi ibridi a base di grafene e nanomagneti molecolari per la lettura del singolo spin. MIUR FIRB Futuro in ricerca 2012. Cnr Nano Modena (A. Candini). 2014-2017.

FLASHit. Unraveling ultra-fast photo-induced phenomena at the nanoscale: a joint theoretical and experimental approach. RBFR12SWOJ. MIUR FIRB Futuro in Ricerca 2012. Università di Roma Tor Vergata (A. Marini); Cnr Nano Modena (D. Prezzi). 2013-2016.

GRAF. Frontiere della ricerca sul grafene: comprensione e controllo di funzionalità avanzate. MIUR PRIN 2010-2011. Università di Trieste (A. Morgante); Cnr Nano Pisa (V. Pellegrini). 2013-2016.

MEMO. Imaging Metallorganic Molecules: Scanning tunneling spectroscopy and many-body theory. MIUR PRIN 2012. Università del Salento (G. Maruccio); Cnr Nano Modena (M. Rontani). 2014-2017.

Nuove sfide nel nanomagnetismo molecolare (RBFR12RRPD1). MIUR FIRB Futuro in Ricerca 2012. Università di Parma (S. Carretta); Cnr Nano Modena (A. Ghirri). 2013-2016.

Cnr projects

Nanomax – Nanobrain. Nanotechnology-based therapy and diagnostics of brain diseases. Cnr Progetto Bandiera. Cnr, IT; Cnr Nano Pisa (G. M. Ratto). 2016-2018.

Optoelectronics in graphene-based vertical heterostructures: effects of lattice mismatch and stacking defects on light absorption from THz to infrared frequencies. Cnr Bilateral Projects. CNR-RFBR, RU; Cnr Nano Pisa (A. Tomadin and S. Heun). 2016-2017. Semiconductor Nanowires: from fundamental studies to innovative devices. Cnr Bilateral Projects. CNR-RFBR, RU; Cnr Nano Pisa (L. Sorba). 2015-2017.

SPM Investigations of superconducting hybrid systems. Cnr Bilateral Projects. CNR-CNRS, FR; Cnr Nano Pisa (F. Giazotto). 2015-2016.

Tuning correlated transport and localization in low dimensional electron systems with spin orbit interaction. Cnr Bilateral Projects. CNR-RFBR, RU; Cnr Nano Pisa (S. Roddaro). 2015-2017.

Regional projects

CAPSULIGHT. Realizzazione di una capsula robotica a LED per il trattamento dei disordini gastrointestinali. Regione Toscana. Cnr Nano Pisa (A. Sgarbossa). 2016-2018.

DIAMANTE. Diagnostica molecolare innovativa per la scelta terapeutica personalizzata dell'adenocarcinoma duttale pancreatico. Regione Toscana. Cnr Nano Pisa (R. Bizzarri). 2016-2018.

DIAST. Sviluppo di un sistema diagnostico integrato per applicazioni spaziali terrestri. Regione Toscana. Cnr Nano Pisa (M. S. Vitiello). 2016-2018.

FELIX. Fotonica ed elettronica integrate per l'industria. Regione Toscana. Cnr Nano Pisa (L. Sorba). 2016-2018.

FLIMFLOW. Fluorescence lifetime multiples flow cytometry system. Biophotonics Plus Joint Initiative. Regione Toscana. Seco S.r.l.; Cnr Nano Pisa (R. Bizzarri). 2014-2016. www.biophotonicsplus.eu

GR-2011-0235-1049. Min. Salute: Bando 2011-2012 Progetti Giovani Ricercatori. Regione Toscana. Cnr Nano Pisa (R. Bizzarri). 2014-2017.

NIPROGEN. La natura ispira processi innovativi per lo sviluppo di impianti per la medicina rigenerativa a elevato grado di vascolarizzazione e performance meccaniche. Regione Emilia Romagna Bando POR-FESR 2014-2020. Cnr Istec (A. Tampieri); Cnr Nano Modena (A. Alessandrini). 2016-2018.

SCIADRO. Utilizzo di flotte e sciame di droni dotati di sensori e tecnologie abilitanti innovative per la sicurezza del territorio e degli aeroporti. Regione Toscana. Cnr Nano Pisa (F. Giazotto; M. S. Vitiello). 2016-2018. BRIC-INAIL. Metodologia di analisi dell'esposizione ai nanomateriali ingegnerizzati integrata alle tecniche di Control Banding per la gestione del rischio nei luoghi di lavoro. INAIL. Cnr Nano Pisa (L. Sorba). 2016-2017.

Meccanismi biomolecolari nella malattia di Krabbe: utilizzo di tecniche nano-biofisiche innovative per l'individuazione di nuovi target terapeutici. Fondazione Cassa di Risparmio di Lucca. Cnr Nano Pisa (M. Cecchini). 2012–2016.

Nanolab 5. Potenziamento laboratori Cnr Nano Modena. Fondazione Cassa di Risparmio di Modena. Cnr Nano Modena (E. Molinari). 2015-2016.

Nanotecnologie per la determinazione di marker molecolari tumorali e per la diagnostica precoce. Fondazione Pisa Bando 2016. Cnr Nano Pisa (G. M. Ratto). 2017-2020.

Role of dysregulated astrocyte-GABAering interneuron interactions in the control of seizures in monogenic models of epilepsy. Fondazione Telethon. Cnr Nano Pisa (G. M. Ratto). 2012-2016.

Sviluppo di materiali e trattamenti/ricoprimenti superficiali per componenti metalliche esposte ad ambienti aggressivi. Fondazione Cassa di Risparmio di Modena "Bando Ricerca Applicata 2013/2014". Cnr Nano Modena (S. Valeri). 2014-2016.

2016-2017 funding chart





Publications

A list of publications from journals with IF \geq 8.462 (i.e., Physical Review Letter's IF in 2016) ordered by their JCR 2016 IF is given. A full and updated list of publications is available on the Institute website at the page "Publications" (www.nano.cnr. it/?mod=men&id=103). Publications marked with © earned a cover in the corresponding journal. Covers are displayed at the end of this section.

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Cnr Nano Life

Cnr Nano events in 2016



FFBRUARY **Graphene & Coffee**

Why is graphene the material of the future? On February 16, V. Tozzini was invited at the "Firenze CaffèScienza" series to talk about graphene, its exceptional properties and the great expectations it triggered in the scientific community.



FFBRUARY Cnr Nano gets 3 ERC grants

Cnr Nano obtained the extraordinary result of having three researchers awarded with the ERC Consolidator Grants, the European Research Council funding that supports pioneering projects and the most creative mid-career researchers. Among 2,051 proposals submitted all over Europe, only 302 were awarded, and our A. Camposeo, S. Corni, and M. S. Vitiello were among them!



MARCH

Cnr Nano technique to light up European industry

An important outcome of Cnr Nano's ERC project "Nanojets", led by D. Pisignano, appeared in the EU official magazine 'Cordis': the project's new cost-effective method of fabricating high quality light-emitting fibres, a result that might represent a benefit for sectors ranging from sensors to wearable smart devices, was highlighted in the European projects' magazine.

APRIL A challenging Cecam Workshop

"Ultra-fast phenomena in quantum physics: a challenge for theory & experiment", (April 11-15, EPFL, Lausanne, CH), organized by D. Prezzi and colleagues, gathered theoretical and experimental materials scientists studying the dynamics of photo-induced electronic excitations in a variety of systems and time-scales to discuss the most recent advances and the main open problems, as well as to foster the collaboration in this novel, wide and fragmented field.



APRIL **Our research on tv**

Our labs in Pisa were in the spotlight of MEMEX, the science TV show of the RaiCultura channel. The episode dedicated to "Investigating and designing materials" included long footage of our laboratories and interviews to our director L. Sorba and to M. S. Vitiello, leading expert on quantum cascade and TeraHertz lasers.



MAY Introducing Majorana's mistery

Cnr Nano participated to the presentation of "No one will find me - Majorana Memorandum", a docufilm by Egidio Eronico about Ettore Majorana, the Italian physicist who inexplicably disappeared at 31 on March 26, 1938. The film was on screen in 4 cities (Firenze, Pisa, Modena, Reggio Emilia) and was introduced by the film director with our researchers who talked about its scientific contents of Majorana's scientific legacy.

Cnr Nano events in 2016



JUNE Promising Phosphorene

ResearchItaly, the web portal of the Italian Ministry of Education, University and Research (MIUR), reports on Phosphorene, its promising properties and the ambitious research project PHOSFUN that involves S. Heun and other Cnr Nano scientists.



JUNE Organic electronics shows off

Cnr Nano and fellow Cnr institutes organized the 3rd edition of the workshop 'Surfaces, Interfaces and Functionalization Processes in Organic Compounds and Applications' (SINFO, University Federico II of Naples, June 27-29). It was a great opportunity to share the latest ideas on the properties of organic semiconductors at interfaces, hybrid systems and bio-functionalized surfaces, and their future implementation into working devices. During the workshop, the exhibition "Elettronica di Plastica", dedicated to bioelectronics, biosensing, electro-optical systems, energy conversion, advanced electronic devices was inaugurated.



JUNE Spinning it right round

The biennial "Conference on Electrospinning" has gained in the years a leading position for the discussion of the most recent scientific and technological advances in the interdisciplinary areas of electrospinning, polymer nanofibers, and related applications. The 2016 event, organized by D. Pisignano in Otranto, IT (June 28- July 1), was the venue for discussions ranging from material development, to applications in tissue engineering and biomedicine, to smart wearables to new materials for energy harvesting, management and storage.

F Nanotech Filiera Business

Il mondo ultrapiccolo non ha più limiti

JULY

Nanotech excellence

Nova24, the technology and innovation magazine of the leading Italian economic newspaper Sole24Ore, presented a special focus on Nanotech business, investments and research. The featured article highlighted the high quality of Italian research in nanotechnology and credited Cnr Nano Modena as one of the European centres of excellence in nanotechnology research.



SEPTEMBER Sowing seeds (of scientist)

Cnr Nano Institute launched the SEED call, in order to fund one-year innovative projects proposed by its young researchers. Among 12 proposals submitted and reviewed by an international panel of scientists, 4 were awarded with a grant. The recipients, A. Ghirri, G. Brancolini, V. Zannier, and F. Telesio, are called to run the project from both the scientific and the management point of views.

Cnr Nano events in 2016

Scienziati e ricerca «Noi, cervelli non in fuga» di Giovanni Caprara a cadioa 21

I cervelli non in fuga: crediamo nell'Italia

La notte europea dei ricercatori e quattro storie di nostri scienziati «La burocrazia si può sconfiggere Anche qui siamo competitivi»

OCTOBER Fighting the brain drain

Andrea Camposeo was interviewed in the major national newspaper Corriere della Sera as a bright example of a scientist able to attract funds to Italy to perform cutting-edge research, and Miriam Vitiello was one of the recipients of the International Award entitled to Guido Dorso, a prize that wants to highlight the work of young researchers of Southern Italy.



OCTOBER ULTRAQCL meeting in Pisa

Cnr Nano organized and hosted in Pisa the EU ULTRAQCL 12 month project meeting. ULTRAQCL is a EU Horizon 2020 research and innovation programme project aiming at using THz quantum cascade lasers (QCLs) as a foundational semiconductor device for generating intense and short THz pulses whose Nano unit is led by M. S. Vitiello.



NOVEMBER Sharing ERC experience

Cnr Nano researchers M. S. Vitiello and S. Corni presented their experience as ERC grantees at a Cnr national meeting in Rome dedicated to train our scientific community in European research council opportunities.



DECEMBER Morphing graphene

A focus on hydrogen storage in graphene studies by K. Kakhiani appeared on Platinum, a magazine of Italian newspaper Il Sole 24 Ore. Kakhiani is a Georgian scientist who works in Pisa with Cnr Nano researcher V. Tozzini thanks to a Marie Sklodowska-Curie grant.

DECEMBER Research can give real hope

Our researcher G. M. Ratto participated in the popular "Telethon marathon", a televised fundraising event for research into genetic diseases. Ratto's team studies the biophysical mechanisms underlying the synaptic plasticity of the brain, in physiological and pathological conditions, in particular in monogenic epilepsy and in Rett syndrome. Ratto offered the audience a message of hope coming directly from research and labs, a real testimony of scientific responsibility towards those who face genetic diseases every day.

Cnr Nano events in 2017



FEBRUARY Into the Future

Starting from Feb. 1, Cnr Nano Modena opened its doors to many high-school students who embarked in a journey of discovery of science and technology, thanks to a guidance project (Into the Future) for high schools, aimed at showing what a career in science is like and what researchers actually do. About 180 students had the chance to enter labs, learn some science where it is actually done, try some experiments, meet people who work in science, listen to stories, and make questions. Hopefully they did fall in love with science after such a close encounter.

FEBRUARY In the interest of science

On the occasion of the "International Day of Women and Girls in Science" declared by United Nations, in a featured interview Elisa Molinari spoke about gender equality in scientific research. She argued that we need the commitment of all to promote women's careers in academia and research. A few weeks later, on the occasion of the International Women's Day, in a Rai Radio1 interview Molinari again stressed the important contributes brought to scientific enterprise by women and added: "Having more wo-



men in science labs is not only a way to give women new opportunities but also a way to enhance the working environment and the scientific research itself.

FEBRUARY Quantum technologies on the spotlight

A well-attended Institute workshop on Quantum Technology took place in Florence, on February 21, to review the ongoing activities in the areas of quantum information, sensing and metrology, and similar. The workshop was also meant as an occasion to develop a common strategy in view of the forthcoming European calls within the Quantera network and the Quantum Technologies Flagship.



APRIL Yambo computing

Combining invited keynote talks, lectures and hands-on sessions, the Cecam workshop "Advanced computing of excited state properties in solids and nanostructures with Yambo", (April 24-28, EPFL Lausanne, CH) provided a balanced training both in the fundamental theory of electronic and optical excitations as well as practical strategies for computation of such challenging systems within a massively parallel environment. The workshop was organized by D. Varsano and colleagues in the frame of the EU MaX Centre of Excellence.



MAY Phosphorene and 2D Companions

Two years after the "Fosforene day" in Florence (17.07.2015), Cnr Nano and other Cnr institutes organized a new workshop about this amazing 2D material in Rome at the Cnr headquarter on May 8. The study of black phosphorus in last two years has registered many successful achievements from the chemistry, material science, and physics point of views, and still there is a lot of work to do.



Approaching the exascale

E. Molinari was hosted by Smart City, a radio broadcast dedicated to innovation, to uncover the frontiers of supercomputing. The forthcoming jump to the exascale computing will allow simulating changes to the electronic structure of materials and thus lead to design materials never seen before, Molinari said. This materials' simulation is at the core of the MaX European Centre of Excellence coordinated by E. Molinari for Cnr Nano.

MAY

Highlighting light-matter coupling

S. Zanotto's PhD thesis "Intersubband polaritons in photonic crystal cavities" was published and highlighted on META Publishing, an open access platform dedicated to Electromagnetics and Photonics. Zanotto, who works as a researcher at Cnr Nano in collaboration with Scuola Normale Superiore, demonstrated how to realize the strong light-matter coupling in a photonic crystal resonator, a tool that holds great promises for the next generation of mid-infrared light sources.

JULY

A bright Junior Professor

Congratulations to our PhD graduated C. Cocchi who was appointed Junior Professor of Theoretical Physics at the prestigious Humboldt University in Berlin. Scientifically grown in Modena, Caterina's research activity will focus on the theoretical study of the interaction between light and low dimensional materials.

Cnr Nano events in 2017



JULY The beauty of the microscopical world

Our fellow scientists G. C. Gazzadi, V. Grillo, S. Frabboni and F. Venturi won with this image the Royal Microscopy Society Scientific Imaging Competition. They were awarded in the Physical Science section with this image named 'Zeroth order diffracted intensity of a structured electron beam generated using a focused-ion-beam-prepared holographic aperture'.



AUGUST Advancing the S&T of Electrospinning

The special issue of "Macromolecular Materials and Engineering" (vol. 3, issue 208) was guest-edited by L. Persano, A. Camposeo, and D. Pisignano, and collected contributions from leading groups in the electrospinning field, in order to provide an overview of the most recent findings in the field from laboratories and companies in 13 countries.



SEPTEMBER As transdisciplinary as photobiology

The 17th congress of the European Society for Photobiology was organized by Cnr Nano in Pisa (4-9 September). It fostered the dissemination of new research and technological development in the transdisciplinary field of photobiology. It encompassed scientific, technological and medical aspects, impacting the civil society, through dealing with light-driven processes related to, e. g., disease diagnosis and treatment using light, photodynamic therapy, DNA damage and repair, environmental safety, climate change, UV effects on plants, crop production, photosynthesis, phototechnology.



SEPTEMBER Solvay 1927 - Trento 2017: women and physics

Ninety years after the famous photo that portrayed 28 male scientists and only one female scientist (Marie Sklodowska Curie) at the Solvay Congress, the University of Trento and the Italian Physical Society took a similar picture it with reversed roles: 28 Italian female physicists, among them E. Molinari from Cnr Nano, and only one single male physicist. With the talk "Rethinking individual paths and evaluation of the research: a critical point of view" E. Molinari participated in the round table "Physics, singular feminine", held during the Italian Physics Society SIF congress.

SEPTEMBER Revolutionising electron microscopy

A Kick-off Meeting hold on October 2-3 in the beautiful Museum Palace in Modena launched the EU FET Open Q-SORT Project. Dedicated to bringing a new measurement paradigm in Electron Microscopy, the project is funded by the European Commission under its highly competitive Future and Emerging Technologies Programme to the tune of 3 million Euros, and is coordinated by V. Grillo from Cnr Nano.



SEPTEMBER A wonder-full night

Last September 29 all over Europe scientists and public met to talk science. Games, experiments, questions, videos, and above all a lot of fun: this happened around 30 countries and over 300 cities in Europe. Cnr Nano was part of it with booths organized in Pisa and Modena and hundreds of people had the chance of seeing and learning that researchers are ordinary people with extraordinary jobs.

OCTOBER Weyl Fermions talking

F. Taddei and colleagues organized at ICTP Trieste the 'Conference on Weyl Fermions in Materials' on October 23–27, attended by the main experts in the field of Weyl-semimetal physics to discuss the most recent theoretical and experimental developments. The meeting also provided a comprehensive overview to scientists wishing to enter this field.



OCTOBER

Unveiling caloritronics

In a perspective article in the journal Nature Nanotechnology, F. Giazotto and A. Fornieri illustrated the opportunities and challenges of phase-coherent caloritronics, an emerging field of nanoscience based on the ability to control and manipulate heat currents thanks to the long-range phase coherence of the superconducting condensate.



NOVEMBER #weareHPC

A Cnr Nano group of female researchers and staff proudly participated to the #WeAreHPC Twitter campaign organized and promoted by Women in HPC in an effort to ensure the greater HPC sector is inclusive and welcoming to all communities. The campaign aimed at showing the many faces of HPC and raise awareness of the essential role of diversity and inclusion.



People

Cnr Nano researchers

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Gender balance in Cnr Nano 2016-2017

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