ELETTRA HIGHLIGHTS 2012 | 2013

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The Elettra Highlights publication for 2012-2013 continues to underline the interest of our user community in the enhanced capabilities of Elettra, that led to an unprecedented 20% increase in the number of proposals received in the last semester for Elettra as compared to the previous semesters. The increased stability, reproducibility and average brightness of Elettra and the successful development of the new free-electron laser (FEL) source FERMI, the only seeded FEL user facility with full control of polarization currently available worldwide, are the main ingredients of our success.

Last year the users of Elettra were able to take full advantage of the increase in machine stability and reproducibility resulting from the top-up operating mode, the realignment of all magnetic components and the introduction of beam-based alignment. In particular, the increase in thermal stability of the different machine components deriving from the full-energy injection yielded a drastic reduction in component failures. The fraction of users’ beamtime unavailable because of injection into the machine went from the 2.6% to just about 0.03%. The overall machine uptime reached 96.1%, the highest ever recorded at Elettra.

The new beam-based alignment system was routinely used to control the electron beam position with a relative accuracy of 10 microns. The circulating current at 2.4 GeV was successfully increased by 33% to 200 mA thanks to a number of improvements in the vacuum chamber cooling system. Successful tests of the new digital low level RF system prototype and of the eight corrector magnet prototype were carried out, the latter designed to make the position of the source point for the bending magnet beamlines independent of the position and angle of the electron beam in the insertion devices. The deployment of such implements is expected to further increase operation flexibility. Upon users’ request, a hybrid filling mode was utilized for about 10% of the users’ beamtime. In this operating mode a single electron bunch separated in time from the electron bunch train produced by continuous filling allows time-resolved experiments, which utilize the single electron bunch, to be performed in parallel with experiments that exploit the entire electron bunch train and high average intensity of the source.

The superconductive wiggler that will provide photon energies up to 25 keV to the second diffraction beamline for structural biology (XRD2) and the new beamline for high pressure diffraction studies (XPRESS) - under construction in collaboration with the Indian Institute of Science in Bangalore - was refurbished to make it compatible with top-up operations and successfully tested on the storage ring. The development of XRD2 and XPRESS, together with the implementation of the new x-ray fluorescence beamline in collaboration with the International Atomic Energy Agency, will substantially extend the range of facilities available to Elettra users.

In the last year the FERMI project attained a number of ambitious goals in three main areas: 1) The FEL-1 laser line achieved and surpassed the design specifications; 2) FERMI was officially opened to external scientists, with the FEL-1 operating as a user facility; 3) FEL-2 produced the first radiation operating in the two-stages cascade mode using the fresh bunch technique.

In the first area the implementation of the X-band (12 GHz) fourth harmonic linearization system together with the laser heater allowed a substantial increase in the charge stored within the electron bunches. Peak currents of 500-600 A were achieved with a constant time profile of a typical 500 fs duration. This, together with the exploitation of the two new high-energy RF deflectors to optimize the electron trajectories, enabled FEL-1 to achieve energies of several hundreds µJ/pulse. For example, energies up to 400 µJ/pulse are now routinely achieved at 52 nm, corresponding to $10^{14}$ photons/pulse, exceeding design specifications. In fact design specifications for FEL-1 where achieved or surpassed throughout the operating wavelength range and down to the minimum design wavelength of 20 nm, and useful intensities from FEL-1 were produced down to 10 nm.
The FEL-1 facility was officially opened to external users and - as a result of the first two calls - a total of 75 proposals were received from 14 countries. Based on the proposal assessment by the international FERMI peer-review panel, beamtime was allocated to 34 proposals, with an average proposer success rate of 45.3%. Several users have indicated that the intensity, wavelength and linewidth stability of FERMI made their experience in Trieste the best ever for them at any FEL facility worldwide. Unfortunately, commissioning of FEL-2 will continue to compete with beamtime assignment to users at least throughout next year. Both our Machine Advisory Committee and our Scientific Advisory Council have recommended to allocate more time to the commissioning of FEL-2.

The electron beam transport line for FEL-2 was completed in January 2012 and this was followed by the installation of the ten undulators produced by our spin-off company Kyma S.r.l. The first stage of FEL-2 is comprised of one modulator and two radiators. The second stage is comprised of one modulator and six radiators. Commissioning of the two-stage FEL-2 facility, designed to cover the 20-4 nm wavelength range, was expected to be a more complex task than commissioning of the single-stage FEL-1. Also, it could be performed only during the shutdown periods of the FEL-1 user facility. First coherent radiation for the first stage of FEL-2 was obtained at 52 nm in May 2012. Coherent radiation from the second stage was obtained at 14.4 nm in October 2012, corresponding to the sixth harmonic of the seed laser (43 nm) in the first stage seeding the second stage at the third harmonic, using the same electron bunch, but a portion of the bunch that was not involved in the first stage seeding process, thanks to a delay line.

The validity of such a technique, denominated Double Stage Cascade High Gain Harmonic Generation (HGHG) with fresh bunch technique, was demonstrated for the first time worldwide in the EUV range at FERMI. Intensities up to 50µJ/pulse were obtained at 10.8 nm (using the 8th harmonic of the seed laser in the first stage and the 3rd harmonic of the first stage radiation in the second stage. Shorter wavelengths will require routine linac operations at 1.5 GeV.

To allow pump-probe experiments, two different strategies were successfully pursued. A 130 meter long laser transport line was implemented to carry to the FERMI experimental hall a portion of the same laser signal used to seed the FEL. This enabled our users to utilize the infrared laser seed laser pulses for jitter-free pump-probe experiments. In addition, during the users’ beamtime on FEL-1 successful pump-probe experiments were carried out using a novel scheme in which a double laser seed pulse was used to generate two FEL pulses with different wavelengths - by about 0.2 nm - and variable time-delay from the same electron bunch. These experiments have opened major new opportunities for the FERMI user community.

Some of the new strategic directions opening up for us and for our partners will be addressed by the thematic workshops that will take place as part of the XXI Elettra Users’ Meeting: “Coherent x-ray spectroscopy: the dream”, and “New challenges for research on graphene: from growth and state-of-the-art characterization towards industrial applications”. Such workshops will serve the purpose of engaging a broader user community, and our partner institutions will have prominent roles in the above events.

We take this opportunity to thank our employees, our Partners and external Users for their enthusiasm and dedication over the years. We trust that with their help we will be able to meet the major challenge of fully exploiting an upgraded Elettra light source while developing the new FERMI free-electron laser source.

Alfonso Franciosi
Chief Executive Officer
Sincrotrone Trieste S.C.p.A.
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Homogeneous growth of one-dimensional Sn-filled carbon nanostructures on indium tin oxide

Vertical or spaghetti-like hollow carbon nanostructures were obtained on glass covered with transparent metallic Indium Tin Oxide, with no addition of external catalytic particles. Chemical vapor deposition of C$_2$H$_2$ between 820 K and 940 K produces nanostructures filled by Sn metal. The carbon skin can be removed by annealing in oxygen atmosphere, living pillars of SnO$_x$. This approach will be a promising path to enhance the efficiency of devices for energy generation and storage, which could benefit from the improved charge transport in absence of grain boundaries or interface contacts.

Indium Tin Oxide (ITO) is the most relevant transparent conducting material instrumental in many applications. Thin layers of ITO are widely used as transparent coatings and electrodes, i.e., in organic solar cells, flat-panel displays, antireflection coatings, radiation protection, lithium ion battery materials and organic light emitting devices, because of their low resistivity, strong absorption at ultraviolet wavelengths, high transmission in the visible and strong attenuation in the microwave region. The possibility of developing techniques to fabricate homogeneous, complex and aligned one-dimensional (1D) nanostructures on ITO using a bottom-up growth approach would represent a significant advance in the above mentioned application fields of transparent conducting materials, paving the way for new architectures of electronic and optoelectronic devices. Indeed, it is extremely important to develop scalable methods that selectively form and orient nanostructures by controlling shapes, aspect ratios and crystalline arrangements, as well as to be able to create electrical contacts between the nanostructures themselves and the substrate, reducing as much as possible the number of possible interfaces since they represent barriers for charge conduction.

By means of chemical vapor deposition (CVD) of C$_2$H$_2$ with the substrate in temperature range 820 < T < 940 K we are able to grow vertical hollow carbon nanostructures filled by metal or metal-oxide nanostructures on ITO-covered glass, with no addition of catalytic particles. Due to the peculiar growth method, the substrate itself works as a built-in bottom contact for the vertical 1D architecture. This is a completely new approach to the problem. Moreover, the strategy is versatile and adaptable to any substrate material on which the ITO can be deposited and treated at the nanostructure growing temperatures, and the lack of external catalysts allows for a rational and simple control of the growth process.

![Figure 1](image_url)

**Figure 1.** a) SEM cross section image of the sample measured at ESCAmicroscopy (top) and the photoemission spectra (bottom) taken in three different points indicated in the SEM image. b) The bottom panel shows an high resolution SEM image of the hollow carbon nanostructures grown at 940 K. The external skin of carbon is visible, while the internal part is made of a denser material (metal). The top panel reports the Raman spectra of pristine ITO and carbon nanostructured ITO. The growth of sp$^2$ graphite-like defected carbon structures is shown by the presence of the D and G bands. Adapted with permission from Carbon DOI:10.1016/j.carbon.2013.07.032. Copyright 2013 Elsevier.
growth process over large areas. Figure 1a shows the cross section scanning electron microscopy (SEM) image of a sample with vertical carbon nanostructures grown on ITO/glass at 940 K (top) and the photoemission spectra taken at the ESCA microscopy beamline (bottom) in three different points. The In 3d peaks appear only at the interface between the nanostructure and the ITO substrate (point c), while for spectra taken along the body (point b) and at the head (point a) of the nanostructure solely carbon is visible. A more detailed SEM image is shown in Fig 1b with a zoom of the vertical nanostructures, which clearly evidences that the pillars are formed by a solid core covered by a skin of a different material. The outside skin is made of carbon, as demonstrated by very surface sensitive photoemission microscopy and also by Raman (top panel in Fig. 1b) measurements, while the internal part is made of metal. The thickness of the carbon layer is ~12±1 nm and according to Raman it consists of disordered sp² carbon sheets.

Fig. 2a shows the photoemission spectra of In 3d and Sn 3d peaks. After the C₂H₂ CVD treatments In remains in the oxide state while Sn splits in oxide and metallic state. Therefore, Sn looks like the catalytic seed of this carbothermal reaction. Moreover, the metallic part of Sn is the same after one year of exposure to air, which means that the metal inside the carbon skin is Sn and that it is protected against oxidation. The carbon skin can be removed by exposing the samples to O₂ atmosphere at T > 600 K, leaving only the tin reduced ITO substrate with SnOₓ nanostructured pillars. Examples of nanostructures without the carbon skin are shown in Fig. 2b, and the corresponding photoemission spectra before (green spectra) and after (black spectra) burning of the carbon skin are shown in Fig. 2a. Finally, Fig. 2c shows the optical transmission of the growth nanostructures compared to the pristine flat ITO. While the transmission is attenuated when the nanostructures are covered by carbon, after the carbon removal the transmission recovers and even surpass the ITO, in particular the infrared region. This holds some importance in view of applications of these structures in solar cell electrodes, since a consistent amount of photon-absorption take place in this region of the solar spectrum.

Figure 2. a) Sn 3d (top panel) and In 3d (bottom panel) XPS spectra of pristine clean ITO/glass substrate (red), after H₂ treatment at 940 K (blue) and after the growth of hollow carbon nanostructures (dashed green line), as measured at normal emission (NE). Spectra of the oxygen burned samples (black line) and of the grown hollow carbon nanostructures, after one year of air exposure, as taken at NE (solid green lines) and 60° off-NE angle (green points). b) SEM images of the metal-oxide nanopillars obtained by burning in oxygen the hollow carbon nanostructures grown at 940 K. No traces of C was found using photoemission. c) UV-vis absorption spectra of samples treated with acetylene at 820 K (black curve) and 940 K (green curve) respectively. Solid curves refer to samples presenting carbon/tin nanostructures, while dashed curves refer to the same samples treated with oxygen at high temperatures. Spectrum of pristine ITO/glass substrate is reported in solid red. Adapted with permission from Carbon DOI:10.1016/j.carbon.2013.07.032. Copyright 2013 Elsevier.

Original Paper

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Fuel cells are appealing devices for effective and green conversion of chemical energy into electricity, but crucial technological barriers hinder their application: chiefly durability of key components (interconnects, electrodes, electrolytes). Space-resolved x-ray absorption, fluorescence and photoelectron spectroscopies open unique opportunities for monitoring material changes at sub-μm scales, providing correlative information about: (i) electrode surface; (ii) electrode-electrolyte interface and (iii) electrode-electrolyte-reactant three-phase boundary.

**Cells for in situ work:** we have overcome technical limitations for in situ work in vacuo and soft x-ray transmission by combining mathematical modelling of cell geometry and electrochemistry with state-of-the-art microfabrication (see Fig. 1 for examples).

**Polymer-electrolyte fuel cells (PEFC):** the use of graphite bipolar plates (BPs) in SOFCs impacts both cost and weight: replacing them with thinner, lighter, and cheaper metal foils is appealing, but requires a thorough understanding of corrosion issues. By combining STXM, XRF imaging and μ-XAS, we have investigated the corrosion of Ni and Fe BPs in a hydrated Nafion electrolyte (Fig. 2). STXM reveals notable morphology changes as a result of cell operation and provides quantitative information for the local electrode thickness. Comparison of Ni and Fe images reveals that the Ni electrode edges remain essentially intact while Fe is smeared, as confirmed by XRF line profiles and maps. μ-XAS Ni and Fe L₃ spectra show that no Ni is present outside the electrode, while Fe exhibits a non-uniform material and chemical state distribution in the electrolyte. In particular, the amount of Fe in higher oxidation states increases in the higher-current density zones. Moreover, Fe was found to penetrate and be fixed into Nafion, contributing to the loss of ionic conductivity.

**Solid-oxide fuel cells (SOFC):** high operating temperatures of SOFCs cause serious durability problems. We review recent studies of polymer-electrolyte (PEFC) and solid-oxide (SOFC) fuel cells performed by in situ photoelectron and absorption microspectroscopy, x-ray absorption microscopy and fluorescence mapping. In particular, we concentrate on a selection of degradation modes of the key functional components: (i) deposition of contaminants at SOFC interconnects and electrodes; (ii) material interactions at PEFC electrode-electrolyte interfaces; (iii) polymer electrolyte poisoning; (iv) mass-transport processes and structural changes occurring at the high operation temperatures of SOFC.

Figure 1. (A) Sketch of the main components of scanning x-ray microscope (TwinMic Beamline) illustrating space limitations of the sample stage (b) schematic views of the electrochemical cell, highlighting the electrode fabrication, electrolyte applications and sealing; (c) open cell with electrical connections. (B) Top: scheme of a cell for in situ SPEM work (ESCAmicroscopy Beamline), featuring Cr interconnects and Ni–Cu bilayer catalysts. Bottom: photograph of the sample stage. Adapted with permission from DOI:10.1002/chem.201201313. Copyright 2012 John Wiley and Sons.
problems, due to poisoning (C and S deposition, Cr migration from BP to catalyst) and structural changes, resulting in catalyst deterioration. Here we report two examples of degradation studies: (i) monitoring of C deposition and (ii) localisation of catalyst activity by overvoltage-induced spectral shifts (Fig. 2).

1) Carbon deposition was followed in situ via evolution of the C 1s signal on Ni catalysts and Cr interconnects at 650 °C in 10⁻⁶ mbar 1:1 C₂H₄/H₂O under different electrochemical conditions. C deposits at open-circuit on both materials, while cathodic polarizations sufficient to form Ni⁰ and Cr⁰, cause carbide growth. Switching to anodic polarizations, C is promptly removed from the Ni anode, while some residues remains on the Cr interconnect, with a metal-bonded sp² coordination.

2) Monitoring of local electrocatalytic activity by SPEM is possible because the photoelectron kinetic energy is affected by the local potential: spectral shifts thus measure the overpotential distribution, provided the chemical state of the investigated element does not change. In this study, the local overvoltage of Ni anodes was quantified by comparison with the ohmic shifts of Zr 3d spectra from the electrolyte (Fig. 2), pinpointing the predominance of charge-transfer and mass-transport contributions.

The applications of x ray scanning microscopies and microspectroscopies can contribute unique information to electrochemical materials science of room- and high-temperature fuel-cells, in terms of: 1) assessment of space-dependent processes; 2) rationalization of damaging mechanisms at the sub-μm scale; 3) study of the coupling of electroactive and electrocatalytic materials.

Figure 2. (A) (a) Top: 22x22 μm² Ni image at 853.6 eV; bottom: Ni L₃ μ-XAS spectra taken in the indicated spots; (b) top: 22x22 μm² Fe image at 706.6 eV; bottom: Fe L₃ μ-XAS spectra taken in the indicated spots; (c) line profiles (indicated by the dashed line in the Ni and Fe images) taken across the boundary of the Fe and Ni electrodes after electrochemical treatment: (d) 40x30 μm² XRF maps of Ni (top) and Fe (bottom) L emission at 1014 eV. The white lines in panels (a), (b) and (d) indicate the initial sharp edge of the electrodes. (B) C 1s spectra measured inside the Cr- and Ni patches before and after applying an anodic or cathodic potential of -3 V: cell operated at 650 °C in 10⁻⁶ mbar 1:1 C₂H₄/H₂O ambient. (C) Ni 2pₓᵧ spectra recorded at the Ni/YZS interface during application of the different cathodic polarization (left) and the measured Ni 2p and Zr 3d shifts as a function of applied cell voltage (right). Adapted with permission from DOI:10.1002/chem.201201313. Copyright 2012 John Wiley and Sons.

Original Paper
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Nanoscale control of self-diffusion processes in bimetallic alloys to tailor surface properties

Achieving control of the nanoscale structure of binary alloys to design novel materials with specific properties may yield to improved reaction rates and selectivity in catalysis, tailored magnetic behavior in electronics, and controlled growth of nanostructured materials. Complex self-diffusion mechanisms determining these key properties close to the surface of a Ni-Cu system can be controlled by finely tuning the relative concentration of the alloy constituents, thus tailoring the material functionality and providing a clear explanation for previously observed effects.

In general, achieving control of the nanoscale structure is of paramount importance for the design of novel materials with specific properties, leading to, for example, improved reaction rates and selectivity in catalysis (reduction of carbon dioxide), tailored magnetic behavior in electronics, and controlled growth of nanostructured materials (graphene). For binary alloys, the composition of the material in the surface region is of crucial importance in determining key properties, and is determined by complex self-diffusion and segregation mechanisms of the different atomic components. Close control of these processes would make tailoring of the material functionality possible by finely tuning the relative concentration of the alloy constituents. By means of a combined experimental and theoretical approach, we have studied this issue for the Ni-Cu system, where the above mechanisms were shown to be mostly defined by kinetic rather than energetic effects.

The processes taking place at the Ni/Cu(110) surface have been followed by high-energy-resolution x ray photoelectron spectroscopy experiments performed at the SuperESCA beamline. Starting from a Ni coverage of 0.75 ML, XPS was used to monitor, at selected fixed temperatures, the real time evolution of the Cu and Ni core levels (Fig. 1). After preparation of the Ni ad-layer, the sample temperature was suddenly raised to the selected target value, following a step-like profile. A spectroscopic “movie” of the segregation process was then obtained by analyzing the dependence of the core level signal intensities as a function of time. Due to the finite inelastic mean free path of the photoemitted electrons, upon diffusion of Ni atoms into the Cu bulk the Ni signal is screened by the atomic layers above. In parallel, as the Cu concentration at the surface increases, the Cu signal intensity raises.

Figure 1. Bi-dimensional maps of the evolution of the photoelectron spectroscopy signal from the Cu and Ni 3p core levels upon Ni and Cu segregation as a function of binding energy and time. In the right panel, data are reported for experiments at three selected temperatures.
Cu signal intensities are therefore related to the composition profile of the sample in the direction perpendicular to the surface. In order to obtain quantitative information, we modeled the diffusion process and optimized a set of parametric rate equations to fit the experimental intensities. Ni segregation energy barriers of increasing height were obtained when going deeper into the Cu(110) sample (from 1.2 to 2.0 eV, moving from the first layer to the bulk). In parallel, Density Functional Theory (DFT) ab-initio calculations modeled the most relevant processes, providing from the theory side diffusion and segregation energy barriers (Fig. 2). On the basis of the obtained information it was concluded that: (i) in the absence of a gas phase chemical potential contribution, there is an energy gain when Ni penetrates Cu from the surface to the second layer, whereas no further gain is obtained in going to deeper layers; (ii) the energy barriers that have to be overcome for diffusion into deeper layers are high with respect to the system temperature under realistic reaction conditions for carbon dioxide reduction on a Ni-doped Cu single crystal (T < 550 K), thus indicating the relevance of kinetic limits to the processes; (iii) these barriers vary significantly by changing the Ni concentration, while the energies of the final configurations remain comparable (Fig. 2a with respect to Fig. 2b). This is a key point, showing that the segregation behavior determined by kinetics and ultimately by the Ni–Ni interaction, can be directly controlled by a fine tuning of the Ni coverage. Observations about carbon dioxide heterogeneous catalytic conversion to methanol (in a CO₂+CO+H₂ stream) on a model Ni/Cu(100) catalyst at ambient pressure conditions indicate that controlled nickel doping of the copper surface in the sub-monolayer range accounts for an increase in the turnover frequency up to a factor of 60.

![Figure 2. Alloying paths and barriers calculated by means of ab-inito methods (DFT). (a) decomposition of a Ni ad-dimer. (b) bulk-diffusion at a Ni ad-atom detaching from a 5/6 ML Ni ad-island.](image)

**Original Paper**

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The local atomic structure and chemical nature of Ag nanoparticles capped with allylmethacrylate (AM) was probed by combining SR-XPS, XAFS and TEM in order to obtain a full insight including morphology, atomic and electronic structure. The results suggest a core-shell morphology made by Ag₃S-like shell around metallic Ag cores. An external AM layer is grafted to NPs surfaces through Ag-S bonds. NP size and composition depend on the Ag/AM molar ratio: higher Ag/AM gives larger AgNPs with thicker Ag₃S layer, while the AM grafting mode is essentially unchanged.

Metal nanoparticles (NPs) are promising candidates for innovative technological applications owing to their peculiar chemical activity and unique physical properties. These properties originate from a complex interplay among many competing factors such as NPs atomic and electronic structure, chemical composition and morphology. Moreover, the NPs can be capped and then functionalized with opportune molecules to avoid coalescence and preserve their properties for applicative purposes. In particular, capping with organic ligands is suitable for massive production, maintaining reliable control on composition, shape and size distribution of the NPs. Furthermore, in order to fit targeted applications, the properties of capped NPs can be widely modified acting on the synthesis parameters and/or opportunely selecting the capping agent. As a matter of fact, the interactions at the NP-ligand interface add additional degrees of freedom that may produce new (often unexpected) properties as for the ferromagnetic response observed in thiol-capped NPs of noble metals like Au or Ag. Clearly the reliable description of electronic and chemical structure of the NP interfaces is mandatory to understand their physical-chemical response and tailor potential applications.

The local atomic structure and chemical nature of Ag nanoparticles capped with allylmethacrylate (AM) was probed by combining SR-XPS, XAFS and TEM in order to obtain a full insight including morphology, atomic and electronic structure. The results suggest a core-shell morphology made by Ag₃S-like shell around metallic Ag cores. An external AM layer is grafted to NPs surfaces through Ag-S bonds. NP size and composition depend on the Ag/AM molar ratio: higher Ag/AM gives larger AgNPs with thicker Ag₃S layer, while the AM grafting mode is essentially unchanged.

Combined XPS and XAFS data coherently demonstrate a core-shell Ag-NP structure, made by metallic (Ag⁰) core, surrounded by a thin shell of Ag₂S-like structure, the AM molecules being grafted to NPs external surface by S providing Ag-S-AM bridges. The Ag₃S-XPS and Ag-K edge XAFS data point out that a larger fraction of Ag is in metallic phase (Ag⁰), while a smaller fraction is bonded to S. More interesting are the information concerning the S electronic state (XPS) and local structure (XAFS), as they provide details about the NP surface regions, namely the shell and NP-AM interface. S₂p-XPS (Fig. 1a) individuated three phases containing S: an Ag₂S-like one, forming a thin shell around the metallic Ag core, the interface region, in which S bridges Ag and capping chains, and finally a fraction of S physisorbed to AM molecules. In particular the S-K edge XAFS data analysis (Fig. 1b) provides structural details about these phases: neighbour atoms type, number and distances. The synthesis route affects the morphology of these NPs: while the fraction of S bonded to AM is largely unchanged raising the Ag/AM atomic ratio from 0.25/1 to 2/1, the fraction of Ag₂S-like phase increases from ≈ 40% to about 60%, pointing out the growth of shell thickness. Combining Ag-K and S-K XAFS data allows evaluating the NP core and shell sizes: the metallic core radius is smaller in 0.25/1 sample (about 1.5 nm) and larger in 2/1 sample (>6 nm), the Ag₂S-like shell thickness is around 0.4-0.8 nm (thinner in 0.25/1 sample).
data suggest that the interface region, in which AM molecules are grafted to the NP by Ag-S-AM bridges, is relatively rough. HR-TEM (Fig. 1d) data confirmed the core-shell structure; the ED pattern (Fig. 1e) depicts two different crystalline phases, one having fcc symmetry which lattice parameter are in agreement with Ag\(^{1}\) core, the other having Im3m cubic symmetry, likely related to the Ag\(_2\)S shell phase. Functionalized AgNP-AM nanoparticles were successfully synthesized with different Ag/thiol molar ratios and studied exploiting state-of-the-art SR techniques: SR-XPS and XAFS (Ag and S K-edges), achieving accurate information about the chemical structure and composition of the NPs as a function of the Ag/AM molar ratio. XAFS data analysis provided fine details on the local atomic structure (interatomic distances, coordination numbers, chemical phases). XPS technique allowed us to recognize different binding modes of S, which could not be distinguished by XAFS analysis, i.e. Ag\(_3\)S-like and Ag-S-AM. The combined XPS and XAFS study provided precise information on the NPs structure and size. It was observed that NP size and composition depend on the Ag/AM molar ratio: higher Ag/AM gives larger AgNPs with thicker Ag\(_2\)S layer, while the AM grafting mode is essentially unchanged.

**Figure 1.** a) S\(_{2p}\)-XPS spectra of AgNPs-AM samples as a function of Ag/AM atomic ratio in the synthesis procedure. The spectral components coming from S atoms in different structures are distinguished by colors: blue/cyan=Ag\(_3\)S-like, red/orange=AM covalently bonded to Ag, green/light green=physisorbed AM molecules. b) Representative example of S K-edge XAFS data analysis: in the bottom panel the experimental data (points) and best fit (red) are reported along with the partial contributions (S-Ag and S-C, shifted for clarity) and the residual (experimental-best fit), shifted for clarity. The Fourier transforms (top) modulus and the imaginary part of experimental (points) and best fit (red). The imaginary parts of S-Ag and S-C contributions are shown, vertically shifted. c) schematic representation of AgNPs-AM core-shell structure d) HR-TEM image: core-shell structure can be observed. e) ED pattern showing two different crystalline phases: AgM and Ag\(_2\)S-like structures. Adapted with permission from C. Battocchio et al., *The Journal of Physical Chemistry C* 116, 19571 (2012) DOI: 10.1021/jp305748a. Copyright 2013 American Chemical Society.

**Original Paper**

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A new anisotropic lattice of Ge quantum dots embedded in amorphous alumina was produced by magnetron sputtering deposition. A specific deposition geometry with oblique incidence of Ge and Al$_2$O$_3$ adparticles was used to achieve the anisotropy. The observed quantum dot ordering is explained by a combination of directional diffusion of Ge and Al$_2$O$_3$ adparticles and a shadowing process which occurs during deposition as a result of the specific surface morphology. The prepared material shows a strong anisotropy of the electrical conductivity in different directions parallel to the sample surface.

Simple processes for the preparation of regularly ordered lattices of semiconductor quantum dots (QDs) embedded in dielectric amorphous matrices play an important role in various nanotechnology applications. Of particular interest are QD lattices with properties that differ significantly in different directions parallel to the material surface. In our past work we have analysed the preparation and ordering properties of isotropic Ge QD lattices in different amorphous matrices produced by magnetron sputtering deposition. The regularity in the QD positions was achieved by a self-assembly process during the films growth, which is based on surface morphology influence on Ge nucleation places. However, our previous depositions were all performed using a standard substrate stage which rotates during the deposition. This ensures the homogeneity of the films, but the regular ordering of QDs appears in domains, randomly rotated around the surface normal. In our most recent work we examined the ordering in ten period (Ge+Al$_2$O$_3$)/Al$_2$O$_3$ multilayer prepared also by magnetron sputtering deposition but under specific deposition geometry. We used small sputtering targets, a close distance between the target and the substrate, and a substrate stage with specific rotation.

**Figure 1.** Structural properties of the films. (a), (b) GISAXS maps measured for parallel and perpendicular direction of the probing x ray beam with respect to the main direction of the adparticle diffusion (the insets show the corresponding simulations), and (c), (d) the corresponding TEM images of the films cross-sections. (e) GISAXS map of a film deposited under standard isotropic conditions. (f) Structure of the anisotropic QD lattice. It is distorted along the y axis with respect to the ideal BCT lattice, which is shown by light symbols. (g) and (h) Simulations of the QD ordering found by GISAXS analysis. Reprinted with permission from DOI: 10.1107/S0021889813059182 Copyright (2013) IUCr Journals, International Union of Crystallography.
substrate and targets, and a fixed substrate stage (held at a temperature of 573 K) during deposition. Under such conditions, the Ge and Al₂O₃ adparticles coming to the substrate from the sputtering targets have a preferential diffusion direction and a non-vanishing in-plane (tangential) component of their velocities. The growth of the Ge QDs and alumina matrix is not isotropic under such conditions due to the combination of directional diffusion of adparticles and shadowing effects caused by Ge QDs. The result of such deposition is formation of an anisotropic lattice of Ge QDs embedded in amorphous alumina matrix. The details of the QD ordering properties in these films were investigated at the SAXS beamline of the synchrotron Elettra. Different directions of the probing x ray beam with respect to the preferential diffusion direction of adparticles were used. Two specific cases, i.e. grazing incidence small angle x ray scattering (GISAXS) maps taken with the x ray beam set parallel and perpendicular (∥ and ⊥) to the diffusion direction are demonstrated in Fig. 1a and Fig. 1b. The different arrangement of Bragg spots in them demonstrates clearly the anisotropy in the material structure. The anisotropy occurs along the diffusion direction of the Al₂O₃ adparticles. The anisotropy is also nicely visible in the TEM cross-sections of the film (Fig. 1c and Fig. 1d), where the correlation direction of the QD ordering is different for the parallel and perpendicular cross-sections. The GISAXS map of the film deposited under standard, isotropic conditions and using of rotational stage (Fig. 1e) is symmetrical and looks the same for all probing x ray directions due to the existence of randomly distributed domains. The numerical analysis of the GISAXS maps shows, that the resulting ordering in the system is a distorted body centred tetragonal (BCT) lattice, tilted toward alumina target, which is schematically illustrated in Fig. 1f and Fig. 1h. The prepared materials show also a strong anisotropy in their electrical properties. The conductivities measured in directions parallel and perpendicular to the main diffusion direction differ by an order of magnitude (Fig. 2a). Such a big difference is explained by the structural properties of the films. More precisely, the conductivity in QD-based materials is highly influenced by the hoping probability between neighbouring QDs, and it decreases exponentially with the QD separation. The QD separations for various directions, found by GISAXS analysis, are shown in Fig. 2b. Due to difference in QD separations along the paths used for conductivity measurements (Fig. 2c and Fig. 2d), the large anisotropy in the electrical transport properties occurs.

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Unconventional ordering phenomena in copper-oxide superconductors

Ordering phenomena are one of the tell-tales of complexity at work in the high-temperature superconductors. Using a variety of spectroscopic probes – angle-resolved photoemission spectroscopy (ARPES), resonant x ray scattering and diffraction (REXS/XRD), and electron diffraction (LEED) – we revealed an unconventional mechanism of electron-lattice coupling in single-layered cuprates. The resulting surface enhanced charge density wave is here found to emerge out of the unique interplay between the charge and lattice degrees of freedom.

High-temperature superconductivity (HTSC) represents one of the most fascinating yet puzzling phenomena in contemporary condensed matter physics, with a convincing microscopic theory of the pairing mechanism still lacking. Among the various materials exhibiting unconventional superconductivity, the family of copper-oxides – or cuprates – has so far dominated the scene, drawing considerable efforts both on the experimental and theoretical side. A particularly relevant question regards the nature of the normal state, which characterizes the CuO₂ planes above the critical temperature. In the normal state of the underdoped cuprates (around 12% hole-doping) there is evidence for various lattice instabilities, which include different phenomena, such as stripes, checkerboard order, and charge-density-waves. We investigated these phenomena in a family of single-layered cuprates, Bi₂Sr₂−ₓLaₓCuO₆, or Bi2201, as a function of doping and temperature, and using various techniques. Bi-based cuprates are in general characterized by a well-known corrugation of the lattice, also known as supermodulation: in Bi2201 this structural feature, labeled Q₁, has a period of 4 unit cells, and runs along the [110] tetragonal direction (b* axis). We discovered that electron-lattice coupling in these materials triggers a second modulation, but only in a narrow doping range. Figure 1(a) shows the ARPES data on a 11% doped samples, where a new set of bands (see yellow circles) is found, providing evidence for a new structural feature (henceforth denominated Q₂), running parallel to Q₁, i.e. along b*. Interestingly, these bands show an intriguing temperature evolution, highlighted in Fig.1(b,c).

Figure 1. ARPES/LEED results on Bi2201UD15K. (a) ARPES momentum-energy map along the nodal direction Γ→(π, π). (b,c) Zoom-in of (a) showing the temperature evolution of the supermodulated bandstructure. (d) LEED cuts along b* [see also inset of (e)]. (e) Temperature evolution of the Q₁ and Q₂ wavevectors. Adapted with permission from J.A. Rosen et al., Nature Communications 4, 1977 (2013).
The temperature-dependent separation between the bands is controlled by the wavevector of the new supermodulation \( Q_2 \). The latter can be tracked with both ARPES and LEED [see inset of Fig.1(e) and linecut in Fig.1(d)], which consistently reveal its quasi-linear drift from high (\( Q\sim1/12 \)) to low (\( Q\sim1/8 \)) temperature, starting around 150K [see Fig.1(e)], while \( Q_1 \) stays fixed at \( Q=0.25 \).

The ARPES and LEED results – both being electronic techniques – characterize the surface structure of Bi2201 samples. The next crucial question then becomes: are the same features also found in the bulk of the material? In order to investigate this phenomenology deeper in the bulk, we resorted to photon-based techniques, which possess a larger probing depth.

Hard x ray diffraction (XRD) and scattering (REXS) maps have been acquired at \( h\nu=17 \) keV (Mo-K\( \alpha \) emission) and \( h\nu=9 \) keV (Cu-K edge) respectively, as a function of temperature. These results are shown in Fig.2(a-d), and evidence an important new aspect: the new supermodulation \( Q_2 \) is also found in the bulk of the material, and its fingerprint in XRD/REXS is revealed through the presence of elongated rods [rather than the ordinary spots, see legend in Fig.2(b)], corresponding to a charge modulation well-defined in the CuO\(_2\) planes (i.e., along \( Q_b \)) but with poor coherence perpendicular to them (along \( Q_c \)). Most interestingly, the extension of \( Q_2 \) in the bulk does not show any temperature dependence [compare the REXS maps in Figs.2(c,d), taken at 6K and 120K, respectively].

Analysis of possible electronic instabilities revealed that nesting channels of the \( Q_2 \)-modulated Fermi surface could explain the extremal wavevectors observed in ARPES and LEED [see Fig.2(e)].

In this sense, the interplay between nodal (N) and antinodal (AN) nesting mechanisms, together with reduced-dimensionality at the surface, explain the observed behavior as originating from an incipient surface-enhanced charge-density wave (see original paper for more details). Ultimately, we have discovered another manifestation of strong electron-lattice coupling in cuprates, which is found to be an important mechanism even in a material characterized by a complex structure to start with.

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Figure 2. (a,b) X ray diffraction map and pictorial legend of visible structural reflections. (c,d) Resonant scattering maps (Cu-K edge) at low and high temperature, respectively. (e) Supermodulated Fermi surface, with nesting mechanisms (AN/N connectors) highlighted. Adapted with permission from J.A. Rosen et al., Nature Communications 4, 1977 (2013).
Competition Between Pseudogap and Superconducting States of Bi$_2$Sr$_2$Ca$_{0.92}$Y$_{0.08}$Cu$_2$O$_8$+δ Crystals Revealed by Time Resolved Optical Spectroscopy

The phase diagrams of strongly-correlated materials are characterized by a wealth of exotic phases. By determining their relationship it is possible to shed light on the intimate nature of the many-body states of these materials. At equilibrium, the order parameters of the coexisting phases are entangled, being characterized by comparable energy scales. Here we report on a non-equilibrium approach, based on a novel time-resolved optical spectroscopy, to unveil a weak competition relation between the pseudogap and the superconducting phases in cuprate superconductors.

Strongly-correlated materials exhibit rich and complex phase diagrams, characterized by intertwined orders that manifest for different values of the external parameters, such as temperature, pressure, doping and magnetic field. In general, different phases can be independent, can compete or finally one can represent a precursor for the other. The result is that they can either coexist or be mutually exclusive. Addressing the relation between two phases, that from a theoretical point of view is described by a mixed term in a multi-component Ginzburg-Landau (GL) free energy expansion, can provide an advance in the understanding of the unconventional electronic properties of these materials.

In this work we focus on the intriguing problem of the relationship between the pseudogap (PG) and superconducting (SC) phases in superconducting copper oxides. In particular, we studied single crystals of underdoped Bi$_2$Sr$_2$Ca$_{0.92}$Y$_{0.08}$Cu$_2$O$_8$+δ (T$_c$=85 K), in which the debate between a competing order (positive free energy coupling term) is still unsolved. So far, this problem has been tackled by performing measurements in equilibrium conditions. However, in the ground state the coupling between coexisting phases can hardly be observed, for the free energy assumes the minimal value and the contributions related to the different order parameters cannot be disentangled. Hence, we tackle the problem by a non-equilibrium approach based on the time-resolved optical spectroscopy (TROS). We address this fundamental issue by investigating the non-equilibrium

![Figure 1. Time Resolved Optical Spectroscopic data above and below T_c.](image)

(a and b) Time-energy matrices of the reflectivity variations at 100 K (a) and 20 K (b) at low fluence (10 μJ/cm²), taken on underdoped Bi$_2$Sr$_2$Ca$_{0.92}$Y$_{0.08}$Cu$_2$O$_8$+δ crystals (T$_c$=85 K). The data are shown in false color scale. (c and d) Spectral traces Δφ$_0$ of the SVD components at 100 K (k=PG) and 20 K (k=SC), respectively. The insets show the spectrotensoral matrix of the component with the same scale used in (a) and (b). Reprinted with permission from G. Coslovich et al., Phys. Rev. Lett. 110, 107003 (2013).
dynamics of the interacting phases after a sudden nonthermal photoexcitation. The possibility to create a transient nonthermal phase, where only one of the order parameters is selectively quenched, is critical for directly measuring the coupling between order parameters. The dynamics of the order parameters can be probed in real time by measuring the reflectivity variation of the system. A broad spectral range of probing photon energies is needed, in order to disentangle the dynamics of different interacting order parameters, since each phase is characterized by a typical spectral signature in the energy domain. Hence, we explore the dynamics of the optical properties in the 0.5-2 eV spectral region with ~100 fs temporal resolution. The singular value decomposition (SVD) is applied to disentangle the spectrotemporal fingerprints (spectral fingerprints $\psi_k$ and order parameters $\psi_k(t)$) in the non-equilibrium reflectivity data. Experimental results (see Fig. 1) show that at low pump fluence ($10 \mu$J/cm$^2$) the recovery dynamics $\Delta\psi_{PG}(t)$ of the PG component $\Delta\psi_{PG}$ proceeds two times faster once the SC order parameter is established. Furthermore, the amplitude of the PG perturbation $\Delta\psi_{PG}$ decreases by a factor two below $T_c$. These results prove the existence of a coupled dynamics for the PG and for the SC order parameters $\psi_{PG}(t)$ and $\psi_{SC}(t)$. Under the assumption that the PG phase has a broken symmetry, a time-dependent GL approach provides a framework for interpreting the coupling term as a positive (repulsive) interaction (see Fig. 2) between order parameters. A quantitative estimation suggests that the interaction is weak enough for allowing the coexistence of the two competing phases. Our results are consistent with a scenario in which the PG and SC phases coexist below $T_c$ and compete in the absorption of the pump photon energy. TROS allowed for the first time the unambiguous and precise measurement of both $\psi_k(t)$ dynamics by recognizing their spectrotemporal fingerprints with no a priori assumptions. In conclusion, we identify the dynamics of PG and SC phases in underdoped Bi$_2$Sr$_2$Ca$_{0.92}$Y$_{0.08}$Cu$_2$O$_{8+\delta}$ by disentangling their spectrotemporal signatures in the non-equilibrium reflectivity data. The results prove the existence of a weak positive interaction between the PG and SC order parameters. This approach paves the way for further applications of TROS to a variety of complex systems characterized by interacting, yet coexisting phases.

**Figure 2.** Temporal evolution of the order parameters of PG and SC phases. (a) Temporal traces $\Delta\psi_k(t)$ of the first two SVD components obtained at $T=20$ K (data of Fig. 1) and the fit to the set of coupled differential equations (see original paper). The PG component at $T=100$ K is shown for comparison. As a reference, the panels on the right side show the spectrotemporal matrices of each component. (b) Dynamics of the PG order parameter obtained from the time-dependent GL model (see original paper) for the case of three different couplings: repulsive ($W>0$), attractive ($W<0$), and no interaction ($W=0$). The repulsive ($W>0$) case best reproduces the experimental data. Reprinted with permission from G. Coslovich et al., Phys. Rev. Lett. 110, 107003 (2013).

**Original Paper**

In recent years the massless-like linear dispersion of electrons in solids has gathered the attention of the scientific community. In particular, electrons described by the Dirac equation, the so-called Dirac particles, have been observed in graphene and in topological insulators. Both these materials are candidates for forthcoming optoelectronic and spintronics devices. Hence a deep understanding of the electron-phonon scattering mechanism is a key topic to be addressed. In our works we tackle this problem directly in the time domain by investigating the dynamics of the hot Dirac particles.

Mastering the physics of Dirac particles (DP) at the surface of topological insulators (TIs) or in graphene is mandatory for the development of novel devices based on opto-electronics and opto-spintronics. The former focus on the possibility to harvest energy from electron-hole pair generated after absorption of light. Whereas, the latter aim to manipulate the spin carrier density of the spin polarized surface DP in TIs by circularly polarized light. In this context, the discovery of a light-induced persistent charge population in the DP of the prototype TI Bi$_2$Se$_3$ motivated several time-and angle-resolved photoelectron spectroscopy (tr-ARPES) experiments for unveiling the electronic properties hidden at equilibrium. Figure 1a shows the upper part of the Dirac cone at equilibrium, as measured with 6.2 eV probe pulses (4$^{th}$ harmonic of the Ti:Sa laser fundamental at 1.55 eV). Conversely, Fig. 1b reports the transfer of spectral weight from below (blue signal) to above the Fermi level (red signal), after exciting the sample with an ultrashort laser pulse at 1.55 eV (pump) and probing at controlled delay times. We interpret this effect as a thermal modification of the Fermi-Dirac (FD) distribution as induced by the excited electrons after their fast thermalization (~40 fs). The effective electronic temperature $T_e$ and the chemical potential $\mu$ are the two parameters that characterize the FD function. Their temporal evolution is carefully extracted by fitting the energy distribution curves (EDCs) at the

![Image](Figure_1.png)

Figure 1. (a) electronic band structure of the topological insulators Bi$_2$Se$_3$, a black arrowindicates the Dirac point. (b) modification of the tr-ARPES intensity after optical perturbation. Red (blue) signal represents an increase (decrease) in spectral weight due to thermal broaden-ning of the Fermi-Dirac distribution. This is studied in details by analyzing the temporal evolution of the EDCs cut at $k_F$ (green line in b), as shown in panel (c). Image adapted from A. Crepaldi et al., Phys. Rev. B 86, 205133 (2012).
Fermi-wave vector $k_F$, as shown in Fig. 1c for selected delay times between the arrival of the pump and probe beams. In particular, a peculiar positive shift in the chemical potential $\Delta \mu(t)$, resulting from the photodoping of the conduction band after excitation of charges across the band-gap, is resolved. Furthermore, a large increase in $T_\text{el}$, as a consequence of the increase in the average energy in the electronic bath, is clearly observed. The relaxation of such an increase exhibits a characteristic time of $\sim 2.5$ ps and it is justified by the energy exchange with the lattice vibrations. This finding provides important information about the scattering strength between the DP and the phonons.

A similar related subject is given by the coupling between electrons and phonons in graphene since it defines its electronic transport properties. In this material the value of the dimensionless coupling constant $\lambda$ has been subject of various investigations at equilibrium. Once again it is possible to address this question looking at the out-of-equilibrium electronic properties by tr-ARPES using ultrashort high harmonics generated in gas (HHG). The DP in graphene, in fact, localized at the Brillouin Zone boundary and a photon energy larger than 16 eV is thus required to directly map the band structure before and after optical perturbation, as shown in Fig. 2b.

Figure 2a shows the various possible scattering mechanisms between a DP and the phonons. In particular, the optical phonons (OP) in graphene, owing to their large energy ($\sim 200$ meV), can only mediate the relaxation of electrons excited at large energies. Instead, at lower energies acoustic phonons (AP) become the dominant scattering channel. However, for momentum conservation this mechanism is quite inefficient such that a three-body scattering, involving collisions with lattice defects, i.e. supercollisions, overtakes the acoustic phonon decay channel. To quantitatively account for the supercollision effect, a set of rate equations based on the multi-temperature model, describing the energy flow between electrons and optical/acoustic phonons, has been developed. As shown in Fig. 2c, by introducing the supercollision term the relaxation of $T_\text{el}$ is very well described. Furthermore, the model enables to extract the electronic coupling constant for both the optical ($\lambda_1 \sim 0.033$) and the acoustic phonons ($\lambda_2 \sim 0.01$).

Figure 2. (a) schematic representation of the possible electron-phonons scattering mechanisms in graphene, involving optical and acoustic phonons and supercollision. (b) equilibrium and out-of-equilibrium electronic properties of graphene measured with high harmonics generated in gas. The analysis of the Fermi-Dirac distribution provides the relaxation of the electronic temperature, shown in c). A multi-temperature model based on three coupled differential equations well reproduces the $T_\text{el}$ dynamics, and provides us with an estimation of the electron-phonon coupling constant ($\lambda_1 \sim 0.033$, $\lambda_2 \sim 0.01$). Image adapted from J.C. Johannsen et al., Phys. Rev. Lett. 111, 027403 (2013).
Future advancements in device fabrication require the combination of bottom-up self-assembly methods together with top-down patterning techniques. Here we demonstrate a method for preparing a patterned bioactive surface using a bottom-up self assembly technique to form a hierarchical mesoporous silica framework to which enzymes were encapsulated. A lithography process was then used to control the precise location of enzyme activity. Deep x ray lithography allows geometric control over the position of enzymes for the potential use as a biosensor in a microfluidic or lab-on-a-chip type device.

Mesoporous materials represent an important class of nanoporous materials for a wide variety of applications such as energy, sensing and separation. Mesoporous cavities range in size between 2-50 nm and an ordered distribution can be beneficial for efficient functionalisation and stable enzyme encapsulation. Recently, ordered mesoporous materials have been investigated for potential use in functional miniaturised devices for applications such as biosensing or biochemistry. Combining this bottom-up synthesis route with a top-down patterning approach provides methods of forming highly precise, spatially controllable and functional smart platforms for the advancement of device fabrication. Various lithographic techniques have been employed to prepare microdevices which can enable the transport of fluids through microchannels and functionalised surfaces. Advancements in the field of device fabrication are now moving towards using these patterning methods for the localisation of biomolecules for sensing. Combining both of these technologies with self-assembly of mesoporous frameworks has the advantage of providing uniform pore sizes, highly accessible functional surface areas and large pore volumes for a suitable support for biomolecule attachment. Previous studies have shown that mesoporous silica can in fact enhance enzyme stability which potentially allows them to withstand harsher conditions and be reused.

Fig. 1 illustrates two protocols (a-d and e-h) used to prepare Deep x ray lithography of mesoporous silica encapsulated enzymes for micro-device fabrication

**Figure 1.** Two protocols for patterning enzyme functionalised mesoporous silica films; (a) A mesoporous silica film was initially functionalised with APTES. (b) Enzymes were incorporated into the functionalised mesoporous film. (c) The films were exposed to x rays using a mask hence forming a patterned enzyme film (d). The second protocol exposed the APTES functionalised mesoporous film (e) to x rays (f), leaving behind a patterned functionalised surface (g) to which enzymes were later selectively encapsulated and permanently grafted (h). (Adapted and Reproduced by permission of The Royal Society of Chemistry).
patterned mesostructured, enzyme functionalised films. In the first protocol, the mesoporous silica film was first functionalised with amino silane (a) before the enzyme encapsulation (b). Subsequently, the functionalised mesostructure was exposed to x rays which decomposes the biomolecules leaving the non exposed areas active (c). This resulted in a patterned porous film (d). With the second protocol, the amino functionalised mesoporous silica film (e) was exposed to x rays (f), leaving behind a patterned APTES functionalised surface (g). The enzymes were then encapsulated onto the patterned mesoporous film, only locating in the unexposed regions (h). Fig. 2a shows the comparative activity between the exposed and the unexposed films for both protocols described in Fig. 1. High activity indicates that the enzymes have been readily encapsulated and maintain their enzymatic properties. Two control samples showed that both amino functionalisation and the mesoporous framework had low enzyme activity even without x ray exposure. This highlights that the mesoporous framework and the use of the amino-silane functionalisation were necessary for efficient enzyme attachment. Fig. 2b shows laser scan images of a silica film with an embedded organic dye. Areas in black were exposed to x rays while areas in green show the unexposed dye. The pattern was obtained using amino-functionalized mesoporous materials bioconjugated with a luminescent protein used as bio-marker (i.e a macromolecular complex of streptavidin and R-phycocerythrin). This experiment confirms the ability of the lithography technique to precisely control the bio molecule functional activity.

The second protocol has the benefit of potentially reducing the amount of enzymes used for bioconjugation as the enzymes will preferentially bind to the amino functionalised areas that were not exposed to x rays. Since the enzymes would not bind to non-specific surfaces, this can minimise the amount of enzymes needed. Combining bottom-up and top-down fabrication techniques offers an exciting synthesis method for future biosensing devices.

Original Paper
C.M. Doherty et al., J. Mater. Chem. 22, 16191 (2012); DOI:10.1039/c2jm32863a

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Figure 2. (a) Enzyme assays show the activity of the mesoporous enzyme films comparing exposed areas to unexposed areas for both protocols. Controls on a non-mesoporous silica surface and a non amino silane (APTES) functionalised surface were performed. (b) A laser scanning image of a film with embedded dye (rhodamine 6G) showing the details of precise patterning. (Adapted and Reproduced by permission of The Royal Society of Chemistry).
High-throughput and efficient surface coverage functionalization of carbon nanotubes (CNTs) is a fundamental challenge to be overcome to fully benefit from their properties. CNTs have demonstrated proof of concept for a large range of applications, including in biotechnology, sensing, separations, energy production or as reinforcements across composite materials. The fine control of the surface chemistry of the CNTs is however critical to optimizing interfaces with surrounding materials or solvents. This is currently limiting large scale CNT manipulation towards commercial products. Although a number of functionalization routes, including gas plasma, gamma ray or ozone have been demonstrated since the early 90’s to efficiently functionalize CNTs, these techniques induce both partial morphological and chemical degradation of the CNTs. The penetration depth of these

**Figure 1.** Representative transmission electron micrographs (TEMs) of CNTs after various treatments: A and B: CNTs after exposure to hard X-ray doses of 262 J cm$^{-2}$ and 8385 J cm$^{-2}$. This is compared to severe damage for CNTs treated by a 10 min and 30 min ozone treatment (C and D) or horn sonication (E).
techniques is also limited to the top 20-50 nm of the exposed surface due either to the thickness of the plasmon or to the reactivity of ozone corresponding to a penetration thickness of a few CNTs only. Given the technological demand of materials with specific functional properties, the controlled functionalization of the CNT side walls is a fundamental step to promote CNTs for the fabrication of novel devices. Here we demonstrated for the first time, the use of hard x rays, from a synchrotron source, for the large scale functionalization of CNTs. We used preformed self-supporting CNT structures, where CNTs are individually entangled in a non-woven fashion, called bucky-paper (BP). BPs were exposed to “white” hard x ray beams (photon energy range at 3–20 keV and a peak at 8 keV) allowing a single step functionalization of the entire thickness of the CNT disks (50 µm). This fast and highly efficient technique takes advantage of the high penetration depth of such high-energy radiation and was used to induce the formation of hydroxyl groups on the CNT outer walls without significantly changing the wall crystallinity (TEM images in Fig. 1). Although the crystallinity of the CNT outer walls was reduced, major damage was prevented, as compared to the dramatic damages induced on the CNT outer walls by other treatment techniques such as ozone or sonication (Fig. 1). The x ray beam therefore solely functionalized the carbon nanotube outer walls and optimum x ray exposure energy between 1048 J cm⁻² and 2096 J cm⁻² has been found to achieve maximum hydroxyl group density. A sol–gel reaction between a commercial fluoro-silane (FASt13) and the hydroxyl-modified CNTs was performed resulting in an even distribution of fluoride atoms on the carbon nanotube surface, opening the way for the mass production of functionalized carbon nanotubes. The plateauing of the contact angle around 145° clearly demonstrates the presence of the fluoro-silane groups on the CNT side walls while the deep penetration of the initial x ray beam exposure was confirmed by similar contact angle behaviour on both sides of the BPs (Fig. 2). Furthermore, from the simultaneous plateauing of both the contact angle and the relative amount of fluoride present on the surface the optimal energy input for this experiment was found to be in the 1040-2096 J cm⁻² range. As determined by XPS, the oxygen content of the x ray exposed CNT BPs was consistently reduced by ~30% after silanisation, corresponding to a significant fluoride surface concentration of 6.13 at%. Higher exposure doses did not further enhance the initial hydroxyl coverage suggesting that saturation was reached over this range of dose matrixes. Finally, the distribution of the hydroxyl groups across the surface of a BP was demonstrated by Energy Dispersive X-ray Spectroscopy. The distribution of the fluoride atoms after grafting is shown to be even and homogeneous across the two BP surfaces which further demonstrated the absence of site selectivity and the large scale applicability of the technique to functionalize CNTs. In conclusion, we have presented a novel and efficient way to functionalize CNTs with hydroxyl precursor groups with minimal damage to the CNT crystallinity. This one-step process allows for subsequent functionalization using the hydroxyl group for molecular grafting. This is the first report of the ability of hard x rays to functionalize CNTs. Notably, medium value x ray doses are sufficient to reach maximum hydroxyl groups surface density and this treatment is shown to be able functionalize through large thicknesses.

Original Paper

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Figure 2. (A: top) Contact angle on the fluorinated samples; black squares and red disks respectively correspond to the face of the bucky-paper exposed to the X-ray beam and to the opposite side; (B: bottom) XPS atomic composition (at%) of the surface of the BP after X-ray exposure and fluoro-silanisation.
There are only a handful of oxide materials that combine optical transparency in the visible region with a high electrical conductivity. This unusual conjunction of properties is exploited in liquid crystal and electroluminescent displays, as well as in photovoltaic cells, where the so-called transparent conducting oxide (TCO) acts as a window electrode. The industry standard TCOs is Sn-doped In$_2$O$_3$, aka ITO. Despite its almost ubiquitous application, several aspects of the physics of In$_2$O$_3$ are still controversial. A striking example is provided by the band gap of In$_2$O$_3$. By using photoemission spectroscopy, a team from Elettra and the University of Oxford have recently determined a value of 2.9 eV, almost 1 eV lower than previous estimates. This important finding points to the existence of a pronounced downward band bending at In$_2$O$_3$ surfaces, giving rise to an electron accumulation layer. This is contrary to the previously established picture of an upward band bending generating a depletion layer. The cause of such electron accumulation has so far remained elusive.

In order to gain further insight on this intriguing system, the high brightness and high energy and momentum resolution of the BaDEIPh beamline was used to acquire photoemission spectra from single crystal thin films of In$_2$O$_3$ grown by oxygen plasma assisted molecular beam epitaxy. The low photon energies used in the measurements ensured a probing depth comparable with the electron accumulation layer thickness. The measured photoemission intensity close to 8° angle-resolved photoemission spectroscopy reveals the presence of a two-dimensional electron gas at the surface of In$_2$O$_3$(111). Quantized sub-band states arise within a confining potential well associated with surface electron accumulation and the surface 2D carrier density establishes that downward band bending for the conduction band must be much bigger than for the valence band. Identification of the origin of the electron accumulation has significant implications in the realisation of devices based on transparent conducting oxides.

Figure 1. (a) Photoemission spectra of In$_2$O$_3$(111) and ITO(111) excited at 19 eV photon energy. The small shift in the positions of the valence band onsets (VBO) between the two samples is indicated. (b) Expanded view of gap states (GS) and conduction band (CB) states close to the Fermi energy. (c) Spectra of the gap state and accumulation layer electrons for In$_2$O$_3$(111) excited at 7-9 eV photon energy. Spectra are normalised using a photodiode to calibrate the photon flux. Collection angle is ± 7° in (a)-(c). (d) Spectra of nominally undoped In$_2$O$_3$(111) excited at $h\nu = 21.2$ eV. Measurements performed after surface preparation by ion bombardment and UHV annealing and then after annealing in oxygen ($1\times10^{-6}$ mbar) for 30 minutes at 600 °C. Adapted with permission from K.H.L. Zhang et al., Phys. Rev. Lett. 110, 056803 (2013).
the Fermi energy for a sample with a bulk carrier density of only $1.5 \times 10^{19}$ cm$^{-3}$ is very much stronger than expected in comparison with ITO where the carrier density is 30 times higher (see Fig. 1a,b). This qualitatively demonstrates the existence of an accumulation layer. Angle resolved photoemission spectroscopy (ARPES) was optimally performed at 9 eV photon energy where the conduction band feature is strongest (Fig. 1c). Interestingly, we found that the intensity of this feature is strongly suppressed by annealing in oxygen (Fig. 1d), suggesting that doubly ionized oxygen vacancies in the outermost ionic layer act as the source of the electrons in the accumulation layer. Theoretical calculations support this picture and demonstrate that surface oxygen vacancies have a formation energy much reduced from the bulk value and also act as shallow donors. The ARPES maps shown in Fig. 2a,b reveal that the electrons confined in the In$_2$O$_3$(111) surface by band bending are quantized into two sub-band states with dispersion parallel to the surface, with a surface carrier density of $4.2 \times 10^{13}$ cm$^{-2}$ as determined from momentum distribution curves at the Fermi energy (Fig. 1c). A detailed analysis using non-parabolic coupled Poisson-Schrödinger calculations indicates that the band bending associated with the conduction band is much larger than the valence band bending, leading to a strong reduction of the band gap at the surface (Fig. 2d). Whereas it is well known that band gap shrinkage takes place in the bulk of highly degenerate semiconductors due to many-body interactions, the effects found here for In$_2$O$_3$(111) thin films are much larger than those observed in the bulk at comparable carrier densities, suggesting that dimensionality plays an important role in determining the band gap width. The implications of electron accumulation for device applications are even more striking than might initially be thought, with not just the presence of a near-surface layer that is highly electron rich, but one that even has an electronic structure fundamentally altered from that of the bulk. However at the same time the ability to tune the surface oxygen vacancy concentration suggests the potential to control the surface electronic properties of ITO and other transparent conducting oxides for applications in electronics and sensors.

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Original Paper


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Alkali Metal Doped Picene Film: Absence of Metallic Phase in a New Organic Superconductor

Thin films of picene and alkali metal doped picene were studied by means of photoelectron spectroscopy and x-ray absorption in order to find a link between the electronic structure and the recently found superconductivity for the potassium doped molecular solid. The absence of a Fermi edge in our data for a thick film of K₃Picene (x = 0 to 3) is a clear evidence that the system is driven by electronic correlations and that correlations make the material always insulating. This is a counterintuitive result since one of the requirement to observe superconductivity is the metallic behavior of the material.

Superconductivity has always been one of the most fascinating topics in condensed matter physics, but breaking the classical ohmic law by controlling quantum effects has not only a pure academic interest. Today, superconductivity is largely used for many applications like powerful magnets, and in the recent years also the possibility of build power lines made by superconductor has been explored. The limitations that superconductors always had are their cost and the necessity of being cooled to very low temperature to make them work properly. The discovery of superconductivity in alkali metal doped fullerenes some decades ago excited the scientific community thanks to the perspectives of build organic superconductors cheaper with respect to the commonly used cuprates. However, for many years this has been an isolated case, until the recent discovery of superconductivity in potassium doped picene and other polycyclic aromatic hydrocarbons compounds. The ability to understand the mechanism that drive superconductivity in these materials will be the route to design organic superconductors as efficient as today’s cuprates, but also significantly cheaper. Both a thin film (one monolayer) and a thick film (multilayer) of picene were sublimated in vacuum on an Ag surface and studied by Ultraviolet Photoemission Spectroscopy (UPS), in order to unveil its electronic structure, and Near Edge X-ray Absorption Fine Structure (NEXAFS) to obtain indication on the geometry of the films. Once collected information on the pristine films they were doped in situ with potassium in various concentration up to K₃Picene (i.e. three potassium atom for each picene molecule), which is reported as the superconducting phase.

Figure 1. Valence band of a multilayer of Picene (black), K₀.₅Picene (red), and K₃Picene (blue), acquired with a photon energy of 31 eV. In the inset (a) the region near the Fermi Level for a multilayer of K₃Picene acquired with a photon energy of 21 eV (black) and 6 eV (red). Dotted lines are the measures performed at room temperature, the solid lines at 19 K. In the inset (b) the region near the Fermi Level for (black) a monolayer of pristine Picene and (red) a monolayer of potassium doped Picene at various doping stages. Adapted with permission from M. Caputo et al., J. Phys. Chem. C 116, 19902-19908 (2012). Copyright (2012) American Chemical Society.
Once again we performed UPS with particular care to the region near the Fermi level, also cooling the sample down to 19 K, i.e. near the 17 K reported as the superconducting critical temperature.

Fig. 1 shows the valence band of the pristine multilayer film (black) and its evolution upon potassium doping (red and blue). The most important variation observed in these spectra during alkali metal doping is the rise of two new states (C and D) in proximity of the Fermi level, but we cannot see any Density Of State (DOS) at the Fermi edge, indicating that the system is always in the insulating state. This is the first indication that K$_3$Picene is a strongly correlated material. The confirmation comes from the inset, where we can see the comparison between the part of the valence band nearest the Fermi level for a K$_3$Picene multilayer film (a) both at room temperature and at 19 K, and for a monolayer at various doping stages (b). In the latter case we observe a DOS at the Fermi levels, which varies with doping, reaching its maximum for K$_3$Picene. The difference in these two systems is the presence of the metallic substrate for the monolayer film, capable to screen the electronic correlation and thus to unveil the conductive phase of K$_3$Picene.

One possible explanation for the absence of metallic phase due to strong correlation interactions in the multilayer may come from its crystalline structure. Fig. 2 shows the NEXAFS spectra for the monolayer film (a) and the thick film (b). The differences between the red spectra (taken with the electrical field of light parallel to the surface, s polarization) and the black one (p polarization, electrical field perpendicular to the surface) permit us to calculate the angle between the surface and the long axis of the molecule. The molecules lie parallel with respect to the surface in the case of the monolayer, while the angle in the multilayer case is 40°, quite different from the reported crystal structure for this molecule. The discrepancy of our crystalline structure with respect to the expected one in a strongly correlated material could induce a phase transition from the superconductive phase to the insulating one, as reported by many theoretical studies.

**Figure 2.** NEXAFS spectra for (a) a monolayer of Picene and (b) a multilayer of Picene. The red spectra are acquired with light in p polarization, while the black ones with light in s polarization. Adapted with permission from M. Caputo *et al.*, *J. Phys. Chem. C* **116**, 19902-19908 (2012). Copyright (2012) American Chemical Society.
Co-phosphate (Co-Pi), Co-borate (Co-Bi), and Ni-borate (Ni-Bi) is a class of recently-discovered metal-oxide catalysts that are based on earth-abundant elements and that have been shown to promote very efficiently the electrochemical splitting of water. They are presently the most promising candidate materials for the anode in artificial leaf technologies, as they are stable, inexpensive, efficient and easily integrable in photovoltaic units. The fundamental origins of their efficiency are presently not well understood. So far, this limitation comes from the lack of a well-defined structural model of these materials. In turn, a precise understanding of the atomistic structure of the active centers governing their function is mandatory for rationalizing experimental findings, for studying the reaction mechanism, and ultimately for optimizing their performances.

Co-phosphate (Co-Pi), Co-borate (Co-Bi), and Ni-borate (Ni-Bi) is a class of recently-discovered metal-oxide catalysts that are based on earth-abundant elements and that have been shown to promote very efficiently the electrochemical splitting of water. They are presently the most promising candidate materials for the anode in artificial leaf technologies, as they are stable, inexpensive, efficient and easily integrable in photovoltaic units. The fundamental origins of their efficiency are presently not well understood. So far, this limitation comes from the lack of a well-defined structural model of these materials. In turn, a precise understanding of the atomistic structure of the active centers governing their function is mandatory for rationalizing experimental findings, for studying the reaction mechanism, and ultimately for optimizing their performances.

Co-Pi selfassembles via electrolysis on conductive substrates from a phosphate-buffered Co\textsuperscript{2+} solution. The resulting catalyst is amorphous as from x-ray diffraction analysis. However, X-ray absorption fine structure spectroscopy (EXAFS) studies show the presence of discrete cobalt-oxo regular molecular units. Their structure is presently debated. Several possible models have been proposed and are compatible with the Fourier-transformed EXAFS spectra. These models, that are far from being realistic and representative of a nanoparticle, are based on clusters of complete and incomplete vertex-sharing cobalt-oxo cubane motifs or on layered edge-sharing CoO\textsubscript{6} octahedra.

In this work we have used the metadynamics computational approach and classical atomistic simulations combined with ab initio methods to propose a realistic and statistically meaningful model of an amorphous cobalt-phosphate catalyst (Co-Pi) that efficiently promotes the photochemical oxidation of water. Our simulations show the emergence of very stable molecular crystallites in the amorphous matrix of CoO nano particles. Our model, supported by simulated extended x-ray absorption fine structure (EXAFS) spectroscopy data, is an important starting point for revealing the working mechanism of these novel water-oxidation catalysts.

Figure 1. a) Free energy landscape of Co-Pi grains in the configurational domain spanned by two collective variables. (b-d) Three grain structures representative of the low-energy basin. Adapted with permission from DOI:10.1021/nn3044325. Copyright 2013 American Chemical Society.
technique combined with ab initio and classical atomistic simulations to demonstrate that ordered Co₃O₄ crystallites can easily form at the surface of amorphous Co-Pi grains. Our Co-Pi grains are very heterogeneous, with the bulk of the grain mostly formed by a disordered Co-O network and phosphate groups localized on the surface.

Empirical potential metadynamics simulations were used to calculate the free energy of Co-Pi grains in the configurational domain spanned by two collective variables. The free energy landscape displays a clear low-energy basin (Fig. 1), which identifies a large number of possible amorphous grain structures. Some of these grains (e.g., grain 3 in Fig. 1d) comprise nanocrystallites consisting of complete and incomplete Co₃O₄ cubane motifs. This suggests a thermodynamic driving force to form such local ordered arrangements of Co₃O₄ octahedra in the amorphous network.

A second set of metadynamics simulations aimed at generating nanoparticles containing a larger fraction of cubane units. Density Functional Theory calculations were used to structurally optimize a selection of these structures. These optimized coordinates were used to simulate the corresponding EXAFS spectra by calculating the phases and amplitudes in the EXAFS equation. The comparison of three relevant grains with the experimental data is shown in Fig. 2. The simulated EXAFS spectra (red and blue lines) of grains containing a large fraction of cubane units present a remarkable agreement with experiment (black lines). Although the fraction of amorphous region in our small nanoparticles might be overestimated with respect to the actual material, regions of our nanoparticles abundant in cubane motifs and terminated by their neighboring phosphate groups well reproduce all the known experimental features of the Co-Pi catalyst.

These results open new opportunities for understanding the functionality of this new class of catalysts. We provide direct evidence of the formation of stable crystallites consisting of complete/ incomplete cubane molecular units. Moreover, our calculations show that these layered cobaltite structures coexist with corner- and face-sharing cubane motifs in the same crystallite. Differently from the idealized models presented so far, the proposed structure provide important information on the crystallite edges, which expose Co ions and incorporate disordered PO₄ groups at the nanoparticle surface.

Figure 2. Upper panel: Simulated Co k⁴-weighted EXAFS oscillation averaged over all Co ions in the grain (red line) and over only the Co ions in the cubane crystallites (blue line). Lower panel: Fourier transforms of the averaged k-space oscillation along with the radial distribution function of all Co ions with all ions in the grain. Adapted with permission from DOI:10.1021/nn3044325. Copyright 2013 American Chemical Society.

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Employment of highly branched copolymer micelles as core substrate to control the soft interactions at the boundary between organic and inorganic domains provides a steric stabilization that enhances the colloidal stability during LTA zeolite formation. Our results, while indicating an interesting possibility in substitution of more traditional templates for the zeolite synthesis, give important insights to the comprehension of the self-assembly processes involved in the development of organic-inorganic mesoporous nanoparticles and for alternative protocols in porous materials production.

In recent years, special efforts have been devoted to develop strategies for the synthesis of supramolecular organic-inorganic nanostructures based on porous materials. The main goal of the different strategies is to achieve a synergy between the properties originating from the porous inorganic substrate and the properties of the involved organic components. Particularly stimulating is the study of alternative protocols for the assembly mechanism of such materials in which a macromolecular template drives the formation of nanostructures with peculiar final properties. Our investigation, performed at the Austrian SAXS beamline of Elettra, outline the self-assembly processes involved in the formation of sub-micron particles of zeolite LTA grown on a polydimethylsiloxane-b-polyethyleneoxide (PDMS-b-PEO) diblock copolymer used as templating agent. The combination of supramolecular interactions, together with the ability to control both the length scale and the structural morphologies, makes block copolymers particularly attractive templates in the synthesis of nonporous materials with new characteristic and properties.

The early stage of the nanoparticles growth process, restricted to an initial time between 1-3 hours, was characterized by the incorporation of the (LTA zeolite) aluminosilicate components into the surface of the nanotemplate with the formation of primary units with a core-shell morphology, while the presence of aggregation processes among primary units led to the formation of extended secondary fractal structures (Fig. 1). Further cross-linking, fusion and rearrangement of the secondary particles leads to the formation of final submicron aggregates as reported in Fig. 2, where the multistep mechanism of formation of the hybrid nano-clusters is proposed. The formation of large supramolecular assemblies at the late stage of

Figure 1. SAXS data during the early stage of the LTA zeolite synthesis are described by a Guinier type analysis (for $q<0.15 \, \text{nm}^{-1}$) as reported in the inset and a core-shell approach (for $q>0.3 \, \text{nm}^{-1}$). Adapted with permission from L. Bonaccorsi et al. Langmuir 29, 7079 (2013). Copyright (2013) American Chemical Society.
the synthesis process was finally confirmed by scanning electron microscopy (SEM) experiments (Fig. 2f), that showed the presence of large spherical nanosized aggregates. The back-scattered SEM image of the system confirmed a condensation of the aluminosilicate components on the aggregates surfaces as proved by the energy dispersive x ray (EDX) microprobe analysis, while x ray diffraction (XRD) experiments indicated the formation of crystalline zeolite LTA, thus confirming the porous nature of the generated particles. Generally, the driving interaction regulating the structure formation in zeolites are difficult to understand, due also to the difficulty to follow (in situ) the time evolution in a multi-component complex environment. In this respect, the use of high molecular weight copolymer template seems to be an interesting possibility in substitution of more traditional templates, as the presence of micellar block copolymers provides a steric stabilization that induces an enhanced (transient) colloidal stability to the synthesis environment. The obtained results indicate how micellar block copolymers precursors offer, from a molecular point of view, favorable conditions for the self-assembly processes involved in the synthesis of hybrid matrices. The soft interaction involved in the sol–gel process as well as the high adaptability to the reaction conditions reveals the very promising properties that polymer based amphiphilic templates can offer in the design and construction of hybrid inorganic-organic functional materials based on zeolites.

Figure 2. Sketch of the self-assembly stages involved during the synthesis of block copolymer templated hybrid nano-particles. The initial association of aluminosilicate species into the corona region of the PDMS-PEO copolymer micelles (a) generates primary units with a core-shell morphology (b). Progressive aggregation process among these primary units leads to the formation of extended secondary fractal structures (c), while further cross-linking, fusion and rearrangement of the secondary particles leads to the formation of final submicron aggregates (d). In the inset (e) the time evolution of the SAXS intensity profile (at T=45°C) after the mixing of the main components is presented, while the scanning electron microscopy (SEM) image of the final nano-aggregates is reported in the inset (f). Adapted with permission from L. Bonaccorsi et al. Langmuir 29, 7079 (2013). Copyright (2013) American Chemical Society.

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Deep Ultraviolet plasmonics in Aluminum Nanoparticle arrays

The onset of LSPRs in metallic NPs and nanosystems leads to the appearance of extremely interesting phenomena. At the LSPR energy, the EM field in the near vicinity of the NP surface is resonantly enhanced, thereby strongly altering the optical response of the nanostructures and creating EM “hot-spots”, which are the basis of ultrasensitive detectors based on plasmon-enhanced Raman spectroscopy. LSPRs are a very general feature of metals, yet the research in plasmonics has mostly focused on the noble metals Ag and Au, due to their low dielectric losses and unparalleled low reactivity. The upper limit to the LSPR energy accessible with these materials, is however the near UV electromagnetic range. This limit can be however overcome with a judicious choice of the plasmonic material. Aluminum is extremely promising in this respect due to the predicted possibility of exhibiting its LSPR in the Deep Ultraviolet (DUV) spectral range. Successfully exploiting Al in plasmonics poses however significant challenges. Aluminum is reactive, hard to synthesize in small-particle form, and quickly oxidizes when exposed to atmosphere, degrading its plasmonic performances and red-shifting its LSPR. Altogether, these technical issues have stood in the way of the full development of Al-based plasmonics, preventing in particular the achievement of the theoretically-predicted DUV limit of the LSPR. In our work, we experimentally tested the limits of DUV plasmonics in ultradense (>10¹¹ particles/cm²) arrays of Al/Al₂O₃ core-shell NPs. We measured the optical response of the Al NP arrays up to 12 eV photon energy, and found the LSPR in the Al NPs at energies of 5.8 eV, by far the highest value reported so far for Al nanostructures. The Al NPs were produced by bottom-up self-organization.

The Localized Surface Plasmon Resonance (LSPR) is a resonant oscillation of the free-electron gas within a metallic Nanoparticle (NP), induced by an external Electromagnetic (EM) field. The widely-employed noble metals, Au and Ag, exhibit their LSPRs in the visible or near ultraviolet spectral range. By choosing Al as the NP material, and by fabricating ultra-dense arrays of small NPs, the LSPR energy has been successfully pushed into the Deep Ultraviolet (DUV) regime, opening new spectral ranges to plasmonics.

![Figure 1. Top left: Schematic representation of the Al nanoparticle array fabrication procedure. Top right: AFM image of the Al/LiF system obtained by the dewetting of a 1.7 nm thick Al film (image size: 800x800 nm²). Bottom: XPS spectra of the Al 2p core level. Adapted with permission from DOI: 10.1021/nn400918n; Copyright 2013 American Chemical Society.](image-url)
approaches (Fig. 1 top left). The systems were fabricated on spontaneously-nanopatterned LiF(110) surfaces, that exhibit a regular ridge-valley morphology with typical periodicity of 25 nm. Grazing-incidence metal evaporation leads to the formation of arrays of nanowires that are thermally dewetted and exposed to research-grade oxygen to form arrays of disconnected Al/Al₂O₃ core/shell NPs.

In Fig. 1, a representative AFM image of an Al NP array obtained by dewetting a 1.7 nm equivalent-thickness Al film (image size 800x800 nm²) is shown. The small agglomerates arranged in “chains” aligned along the nanopatterned LiF surface are Al NPs with mean in-plane diameter of $(17\pm5)$ nm. High-resolution X ray Photoelectron Spectroscopy (XPS) spectra, in the energy region of the Al 2p core level (Fig. 1, bottom) reveal the presence of a metallic-Al core enclosed by an Al-oxide shell. Thus, the small Al NPs retain a metallic core even after strong oxidation, making it possible to observe their LSPR excitation.

In Fig. 2, bottom left, we show the optical extinction of the Al NP arrays as a function of photon energy, measured in normal-incidence at the BEAR beamline, with the electric-field vector aligned either parallel (longitudinal) or perpendicular (transverse) to the Al-NP “chains” (Fig. 2, top). In both configurations, a clear extinction peak indicates the successful detection of the LSPR. In the transverse configuration, the LSPR is found at the strikingly-high energy of 5.8 eV, the highest ever observed in optically-excited metallic NPs. In the longitudinal case, the plasmon hybridization along the NP chains red-shifts the LSPR to the slightly lower value of 4.2 eV.

Theoretical calculations have been performed by different methods, namely Discrete Dipole Approximation (DDA) and Finite-Integration Technique (FIT). FIT (Fig. 2, bottom right), in particular, reproduces the high-energy character of the LSPR excitation, along with the redshift of the longitudinal LSPR induced by the plasmon hybridization along the NP chains. The achievement of a high-energy plasmonic response in Al NPs, and the ease of fabrication of these NPs in ultradense arrays is a milestone for DUV plasmonics, and a promising achievement for future applications in plasmon-enhanced DUV optical spectroscopies.

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Original Paper
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Figure 2. Top: schematic representation of the optical transmission geometry. Bottom left: optical extinction of the Al/LiF NP array in longitudinal and transverse geometries (open and full markers, respectively). Bottom right: FIT calculated extinction spectra. Adapted with permission from DOI: 10.1021/nn400918n; Copyright 2013 American Chemical Society.
We unveiled the mechanism driving the insulator to metal transition in magnetite at the microscopical level by means of advanced time-resolved spectroscopic tools. We demonstrate that it is possible to photo-induce a metal/insulator phase segregation within one picosecond at cryogenic temperatures in magnetite, showing that it is possible to manipulate the electrical and thermal resistivity of prototypical electron-correlated materials at unprecedented speed.

Magnetite is not only the oldest magnetic material discovered by mankind but also belongs to a family of materials whose properties are determined by the non-trivial interactions among its elementary excitations. Typically, the physical properties of a simple crystal, such as its electrical, thermal, and optical properties, can be predicted by means of relatively straightforward calculations that consider independent charge carriers within the system. On the contrary, the properties of a strongly correlated electronic system (SCES) are determined by the interactions among electrons. Generally speaking the theoretical prediction of the physical properties of these system is thus both complex and poor, but on the other hand this class of materials displays a variety of intriguing and spectacular phenomena such as high-temperature superconductivity, magnetic memory effects, and giant magneto-resistance.

Being the electron-electron and electron-boson interaction on comparable energy scales in a SCES, the fine tuning of an external parameter such as pressure or temperature might induce a phase transition between competing phases. This is what happens to magnetite that turns insulating if cooled below 123 K. Such long studied and poorly understood phase transition is named Vervey transition and represents a prototypical model system to address the role of the electronic and lattice degrees of freedoms in a correlation-driven metal-insulator phase transition.

In our paper, recently published in Nature Materials, we address the detailed mechanism underneath the Vervey transition. By approaching the critical temperature \((T_c)\) from above,
magnetite exhibits a dramatic change of its physical properties, undergoes a structural deformation and switches from a metal to an electrical insulator. Several mechanisms involving the role of the electronic, magnetic, and lattice correlations have been invoked in order to rationalize this effect. The first major achievement of our scientific work is that we were able to rationalize the details of the physical mechanism that drives the dramatic evolution of the electrical and mechanical properties at the Vervey transition. We identified specific local structural distortions involving three iron atoms, namely trimerons, whose coherence length is enhanced upon cooling as much as establishing a fully insulating and distorted phase below $T_v$. The second major achievement is that we demonstrate how it is possible to manipulate the physical properties of magnetite by using intense ultra-short laser pulses. Both x rays and reflectivity pump-probe measurements performed below $T_v$ unveiled a novel non-thermal dynamical process above the critical fluence $\phi_{\text{crit}} = 1.3 \text{ mJ/cm}^2$ when laser pump pulses resonant with inter-site charge-transfers between two iron sites ($\sim 1.55 \text{ eV}$) are employed. This can be seen by inspecting Fig. 1, where time-resolved reflectivity measurements are reported for two significative pump fluences below (a) and above (b) $\phi_{\text{crit}}$, respectively. A negative transient reflectivity is shown at lower probe energies and a positive response is present at higher ones. When $\phi > \phi_{\text{crit}}$ the negative part around $E_{\text{probe}} \sim 1.8 \text{ eV}$ is strongly enhanced on the picosecond timescale, as qualitatively expected if the material is entering the metallic phase. This ultra-fast picosecond timescale dynamic is shared by the deformation of the crystal towards the metallic phase structure as detected by x rays experiments (Fig. 2).

In conclusion we identified the critical density of photo-destroyed trimerons above which segregated metallic and insulating phases coexist in magnetite within one picosecond following the electromagnetic perturbation. Being the ultra-fast laser-induced change of the electromechanical properties of magnetite on a much shorter timescale than the fastest graphene-based transistors, our work establishes the switching speed limit in future oxide-based electronic devices.

Figure 2. Photo-induced phase segregation in magnetite. The photo-destruction of the trimerons due to inter-iron pump-induced charge-transfers launches intertwined electron-lattice dynamics (a). At $\phi > \phi_{\text{crit}}$, the holes develop with a time constant of $1.5\pm0.2 \text{ ps}$ (b) to a segregated insulating/metallic phase (c) where the crystalline structure approaches the metallic one (d). Reproduced with permission from S. de Jong et al. Nature Materials 12, 882–886 (2013).

Original Paper
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Surface symmetry-breaking and strain effects on orbital occupancy in transition metal perovskite epitaxial films

Transition metal oxides are nowadays pivotal in many technology and science areas. Strain and interface engineering of thin films open many ways to control the physical and chemical properties of these materials. In particular, the modulation of the electron filling of the d orbitals is known to be crucial for the magnetotransport properties, as well as for determining the chemical reactivity at the surfaces. Taking the La$_{2/3}$Sr$_{1/3}$MnO$_3$ manganite as a working example, we show that the electronic occupancy of the 3d-eg orbitals, i.e. $x^2-y^2$ and $3z^2-r^2$, can be tailored at will by means of strain in thin films and by control of surface atomic termination.

The electron filling of transition metal atom 3d orbitals largely determines many properties of composite materials. Indeed, tailoring their electron occupancy and their relative orientation in crystal lattices has allowed disclosing the tremendous impact that charge and orbital ordering have on the electric and magnetic properties of oxides. This effect is particularly dramatic in manganite-based La$_{2/3}$Sr$_{1/3}$MnO$_3$ (LSMO) oxides where there is a subtle interplay of kinetic, elastic and spin-related energy terms. In thin films strain effects and symmetry breaking at interfaces are expected to further modify the orbital filling and thus the macroscopic material properties. Furthermore, the interface with the vacuum or more generally, the free-surface of transition metal oxides are of major interest in areas like green energy and catalysis. For instance, it has been recently shown that the oxygen evolution reaction, of high relevance in many applications including water splitting, is determined by the degree of filling of the 3d-orbitals, and thus depending on the electron number and spin state of the transition metal at the oxide surface.

Linear Dichroism in the X ray absorption (XLD) is an extremely sensitive probe of the orbital occupancy of the distinct 3d orbitals, which has proven to be successful even at buried interfaces. Linear Dichroism in the X ray absorption (XLD) is an extremely sensitive probe of the orbital occupancy of the distinct 3d orbitals, which has proven to be successful even at buried interfaces.

Figure 1. (a) Sketch of the XAS measurements for incident radiation polarized out of the plane (blue) and in the plane (red) of the samples (b) representation of the surface symmetry-breaking effects inducing a preferential occupation of the orbitals oriented out-of-plane. Purple layers account for MnO$_2$ planes while yellow layers account for (La,Sr)O planes; (c) top: representation of the MnO$_6$ octahedral distortions as a function of strain; middle: subsequent effect of the JT distortion on the $e_g$ levels of Mn$^{3+}$ ions; bottom: Mn L-edge XLD simulated for Mn$^{3+}$ ion in a tetragonal crystal field with $c<a$ (left), with $c>a$ (right) and with octahedral field (centre). Reprinted with permission from DOI:10.1038/ncomms2189.
interfaces. In bulk cubic ABO₃ perovskites the octahedral coordination of cations at B-sites splits the 3d-orbitals into a degenerated t₂g triplet and a degenerated eg doublet with (xy/yz/xz) and (x²-y²/3z²-r²) symmetries, respectively. Further lowering of the crystal-field symmetry breaks the degeneracy of x²-y² and 3z²-r² orbitals (Fig. 1).

In order to explore how the 3z²-r² vs. x²-y² orbital occupancy in (001)LSMO thin films is affected by strain and interfaces, XLD at the Mn L₂,₃ edge has been measured at the BACH beamline. Epitaxial thin films of various thicknesses have been grown on single crystalline substrates creating distinct tensile or compressive strains in the films. Systematic analysis of dichroic data allows determining how band filling changes with strain. By plotting the integrated area of the XLD signal as a function of lattice mismatch between LSMO and substrates (Fig. 2), a clear linear tendency is observed with strain. In agreement with theoretical predictions and earlier works, it is found that tensile (compressive) strain favors x²-y² (3z²-r²) occupancy. However, an additional contribution is found to act on the orbital occupancy, which induces a shift in the plot of the XLD area, towards more positive values, indicating a larger contribution from 3z²-r² than expected. Following the same methodology for tensile strained samples grown on SrTiO₃ substrates, including single terminated samples. Reprinted with permission from DOI:10.1038/ncomms2189.

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Original Paper
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Figure 2. Integrated area of the XLD signal as a function of lattice mismatch between La₂/₃Sr¹/₃MnO₃ and substrates. Negative values indicate preferential occupation of in-plane x²-y² orbitals, while positive values indicate preferential occupation of 3z²-r² orbitals. The dashed line is the expected variation of the integrated area due to strain effect; the arrows indicate the shift induced in the XLD spectra by the free-surface contribution in the thin films (more surface sensitive) with respect to the thick films. In Bottom inset: integration range. Top inset: area under the XLD spectra as a function of thickness for samples grown on (001)SrTiO₃ substrates, including single terminated samples. Reprinted with permission from DOI:10.1038/ncomms2189.
Using sunlight to split water offers a strategy for replacing fossil fuels with clean energy vectors. The overall reaction involves a sequence of light-promoted electron and proton transfers coupled with a rearrangement of molecular bonds, ultimately splitting water into molecular hydrogen and oxygen. The main challenge is finding suitable catalysts for the half reaction of water oxidation ($2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$) that ensure low overpotential (i.e. the extra potential required to oxidize water on top of the thermodynamic value of 1.23 V, measured at pH=0 with respect to the normal hydrogen electrode), high turnover frequencies, and long-term stability. Ideally these materials should be based on earth abundant elements, to ensure very large scale deployment of artificial photosynthesis devices. Several metal-oxides based on precious elements, like RuO$_2$ and IrO$_2$, are known to be good catalysts for water oxidation, and recently also materials based on Co oxides have displayed excellent catalytic properties. The structure and composition of the active sites in these materials, however, are strongly dependent on surface morphology, preparation, and doping conditions, hindering the precise mapping of surface-absorbed species and/or detection of short-lived intermediates. As a result, the mechanism for water oxidation promoted by metal-oxide heterogeneous catalysts such as RuO$_2$ remains not well understood, severely limiting our ability to optimize these materials. In this work we focused on Ru$_4$-POM, a well-defined fully inorganic molecular catalyst. This material has been shown to oxidize water in the homogeneous phase with small overpotential (0.35 V), high turnover frequency (>450 h$^{-1}$), and no degradation. The x ray absorption near edge spectroscopy (XANES) of Ru$_4$-POM has been performed for solid samples on the XAFS beamline at the Elettra synchrotron source. Ru$_4$-POM and hydrous RuO$_2$ display identical XANES edge and line shape. Since the edge position is known to depend on the ruthenium oxidation state, we performed a theoretical thermochemical analysis of water oxidation adopting the computational method proposed by Nørskov and coworkers. The electronic structure of the system was described through density functional theory, employing the B3LYP hybrid functional, and a DZVP Gaussian basis set. The goal was identifying the sequence of intermediates “$S_i$” that, through a cycle of four stepwise proton-coupled electron-transfer oxidations (PCET), make the formation of the O–O bond and the release of O$_2$ thermodynamically favourable. We discovered cycles requiring the active participation of either one or two Ru centers. In both these cycles the energetically most demanding oxidation is the formation of an oxo moiety (Ru(V)-OH $\rightarrow$ Ru(VI)=O + H$^+$ + e$^-$), requiring 1.53 eV and leading to a theoretical overpotential of 0.39 V. This is in excellent agreement with the experimental overpotential for Ru4-POM (0.35 V).
Using metadynamics, we explored the mechanism through which the key O-O bond forms. Starting from an intermediate containing two oxo groups (S6 in Fig.1a) our simulation predicts that the O-O bond is preferentially formed via an intermolecular mechanism, consisting in the nucleophilic attack on the Ru-oxo moiety by a solvent water molecule, which evolves to a hydro-peroxo ligand and liberates a proton in solution. This path is energetically more favorable than any intramolecular reaction mechanism. The free energy landscape as a function of two appropriate collective variables is displayed in Fig. 1b-c. It shows that the nucleophilic attack proceeds via a concerted mechanism, in which the formation of the O–O bond and the deprotonation of the solvent water molecule happen at the same time.

For a wide class of crystalline metal and metal-oxide surfaces, the binding energies of metal-aquo, -hydroxo and -oxo species are shown to depend linearly on each other. As a result, the free energy of each water oxidation step can be expressed as linear functions of the oxygen binding energy ($\Delta E_O$), which is taken as the reaction descriptor. We found that Ru4-POM obeys the same linear relations as the parent oxide (RuO$\textsubscript{2}$), resulting in almost optimal distribution of the overall free energy cost for water oxidation among the four one-electron oxidation steps. This rationalizes the similar performance of RuO$\textsubscript{2}$ and Ru4-POM as well as the fact that their overpotential is the smallest among known water oxidation catalysts.

In conclusion, we have shown that the efficiency of the Ru4–POM complex stems from thermodynamic origins that are common to metal–oxide surfaces and we identified a parallel scenario of water oxidation between two efficient classes of homogeneous and heterogeneous inorganic catalysts. The core of Ru4–POM can therefore be viewed as an optimal RuO$\textsubscript{2}$ cluster in which every metal center is exposed to the solvent and able to catalyze the oxidation of water.

![Figure 1. Mechanism of O-O bond formation: a) Structure of the initial (S6), transition (TS), and final states (FS). Red, white, green, cyan spheres represent O, H, Ru, Cl atoms; b) Free energy surface two CVs obtained from the metadynamics simulation; c) Two dimensional cut of the free energy showing the activation energies obtained with PBE/B3LYP functionals, respectively. Adapted with permission from Figure 5 of DOI: 10.1073/pnas.1213486110. Copyright 2013 National Academy of Science.](image-url)

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**Original Paper**
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Mott physics in a cluster: Optical conductivity of GaTa$_4$Se$_8$ under high pressure supports DMFT predictions

The GaTa$_4$Se$_8$ lacunar spinel chalcogenide is a Mott insulator whose fundamental building blocks are clusters of transition metal Ta$_4$ atoms. Its striking resistive switching properties make it a very promising material for RRAM applications. We have employed infrared measurements at high pressures to address the insulator-to-metal transition in the GaTa$_4$Se$_8$. The very good agreement between data and theoretical calculations performed within the Dynamical Mean Field Theory, underline the almost ideal one-band character of GaTa$_4$Se$_8$.

The band theory of solids provides the framework for the understanding of the insulator to metal transition (IMT) in semiconductors. This is one of the key achievements of the past century, laying the foundations for an epochal technological revolution. Band theory fails, however, in describing the electronic properties of many transition metal oxides with half-filled d or f orbitals.

When the electronic Coulomb repulsion energy $U$, dominates over the tendency towards metallization driven by Kinetic Energy, the conduction band splits into so-called lower (LHB) and upper (UHB) Hubbard bands, and the material is turned into a Mott insulator. In order to recover the metallic state one can either push the chemical potential away from half-filling or increase the bandwidth ($D$), so that the Kinetic Energy gain can now catch up with the Coulomb driven localization tendency. The value of the ratio $U/D$ determines the ground state of the system. Experimental control over the $U/D$ parameter can be achieved through the application of High-Pressure in a Diamond Anvil Cell. Pressure reduces the interatomic distances thereby increasing the wave-functions overlap, and thus $D$.

GaTa$_4$Se$_8$ is a lacunar spinel chalcogenide undergoing an IMT under pressure. A resistive switching induced by electric pulses was discovered in these compounds, making this material promising for RRAM applications. It was argued that GaTa$_4$Se$_8$ may belong to a new class of Mott insulators where the relevant entity for electronic correlation

![Figure 1](https://example.com/figure1.png)

Figure 1. (a) Schematic view of the evolution of the spectral function and of $\sigma(\omega)$ in a Mott insulator and in a correlated metal on each side of a bandwidth-controlled IMT. (b) Drude-Lorentz fit of $\sigma(\omega)$ at 0 and 10.7 GPa. Adapted with permission from V. Ta Phuoc et al. Phys. Rev. Lett. 110, 037401 (2013).
is a cluster of transition metals Ta₄ rather than a single atomic site, and that its striking resistive switching properties are related to a Mott IMT.

We measure the pressure dependent optical conductivity \( \sigma_1(\omega) \) of GaTa₄Se₈. A single broad peak [in red in Fig. 1(b)] centered at 4000 cm\(^{-1}\) is required to fit the infrared ambient pressure \( \sigma_1(\omega) \). By contrast, the simplest fit of the high pressure \( \sigma_1(\omega) \) requires two additional contributions: a narrow Drude peak [in green in Fig. 1(b)] and a midinfrared band at 1500 cm\(^{-1}\) (blue). The change from one mode to three modes at the IMT suggests that GaTa₄Se₈ is a Mott rather than a band insulator. In a one-band Mott insulator, a single excitation is expected between the LHB and the UHB, centered at the energy \( U \) of the onsite Coulomb repulsion, as shown in Fig. 1(a). In GaTa₄Se₈, this excitation is centered at \( U=4000 \) cm\(^{-1}\). On the metallic side of the IMT, theory predicts the appearance of a quasiparticle (QP) at the Fermi level, yielding two new optical excitations: a Drude peak corresponding to QP excitations [in green in Fig. 1(a)] and a contribution at \( U/2 \) assigned to excitations from the LHB to the QP, or the QP to the UHB [in blue in Fig. 2(a)]. Note that from our data, \( U \) does not depend on pressure: this is consistent with the very small compression with pressure of the Ta₄ tetrahedral clusters, since the size of this entity determines the \( U \) value in this compound.

Overall the above analysis rules out a band insulator scenario and provides several striking evidences that GaTa₄Se₈ is a Mott insulator undergoing a bandwidth-controlled IMT under pressure. The bare uncorrelated \( D \) can be calculated through conventional band structure calculations. This allows us to pinpoint our data within a typical \( T/D \) vs \( U/D \) phase diagram from Dynamical Mean Field Theory (DMFT). From Fig. 2, we establish that our room temperature data between 0 and 10 GPa are located in the crossover regime (i.e., above \( T/D=0.04 \)). The onset of metallicity on \( \sigma_1(\omega) \) spectra at 6 GPa is observed at \( U/D_{\exp}=2.05 \) (see Fig. 2), in very good agreement with DMFT, predicting \( U/D_{\text{theo}}=2.35 \) on the right side of the crossover domain.

Such good agreement between data and theory results from the almost ideal one-band Mott insulator character of GaTa₄Se₈. The canonical Mott insulators considered so far (Cr-V₂O₃ or NiS₂-xSeₓ) are comparatively more complex with several active bands around the Fermi energy. In this context, GaTa₄Se₈ could become the new archetypal Mott insulator ideally suited for future comparisons between experiments and theory.

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Original Paper
Double photoionization of Mg has been studied experimentally and theoretically in a kinematics where the two photoelectrons equally share the excess energy. The observation of a symmetrised gerade amplitude, which strongly deviates from the Gaussian ansatz normally used to describe the amplitude, is explained by a type of two-electron interference predicted theoretically, but never before observed experimentally. Similar to the Cooper minima in the single photoionization cross section, the effect finds its origin in the radial extent and oscillations of the target wavefunction. The effect of the target orbital on the photoionization cross-section in the form of Cooper minima has long been established and commonly used to obtain information on the electronic structure in gas phase as well as in condensed matter. Cooper minima are determined by the vanishing radial overlap between the photoelectron wave function and the target orbital. The situation is more complicated in double photoionization (DPI). However recent calculations have predicted that a strong effect of the target electronic structure should be observed in the angular correlation pattern in the two-electron continuum, arising from two-electron interference effects similar to those associated with the well known one-electron “two-slit” experiment. Alkaline earth-metal atoms, “quasi two-electron” systems with the outermost orbital characterized by one or more nodes, represent the most suitable candidates for the investigation of this effect. The DPI process of the Mg atom has been studied at 55.49 eV in equal energy sharing kinematics, where both the electrons in the continuum have a kinetic energy of 16.4 eV. The triple differential cross sections, TDCS=d^3σ/dE_dΩ_1 dΩ_2, measured when one electron is detected at 0° and 60° with respect to the polarization axis of the radiation and their 3D representation are shown in Figure 1.

By considering the invariance with respect to the rotation around the polarization direction of the radiation, the TDCS can be written in a way that allows full separation of the geometrical factors and the dynamical parameters.

Figure 1. The TDCS of Mg at 0° (top) and 60° (bottom) with respect to the polarization axis of the radiation (labeled ε in the figure) are compared to the theoretical predictions of the CCC calculations, which are also used to plot 3D distribution of the TDCS. The red arrow indicates the direction of emission of the fixed electron and hν the photon beam direction.
relevant to the physics of the DPI process. The angular correlation between the two simultaneously emitted electrons is represented by the symmetric, or gerade, $a_s$ amplitude. The experimental $a_s$ amplitude and its comparison with the theoretical one calculated in the frame of the Convergent Close Coupling, CCC model, are shown in Figure 2a. A single Gaussian function has been found to be a useful approximation to describe the $a_s$ amplitude of the DPI of He. In Figure 2 one sees that the central portion of the Mg amplitude, near the mutual photoelectron angle $\theta_{12} = 180^\circ$, can be represented by a single Gaussian, but the fringes of the Mg amplitude cannot. Indeed, the whole of the Mg amplitude can be better described by the di-Gaussian parametrization

$$a_s = G(A, \gamma_1, \theta_{12}) + e^{i\phi} G(A, \gamma_2, \theta_{12})$$

where $\gamma_1, \gamma_2$ and $\phi$ are the correlation width and the complex phase factor, which represents the interference of the two Gaussians. Each Gaussian width may be linked to the radial extent of the target orbital of the singly charged ion, that can be considered to be the target for the first electron ionized by the photon. A more sparse target orbital can be reached by a larger number of partial waves of the electron in the continuum, which leads to a narrower Gaussian. Thus, it is natural to associate the wide and narrow Gaussians, relevant to the present case, with two characteristic regions in the target coordinate space. In the Mg case of a 3s-shell target orbital, there are three oscillations but the first one, near the origin, is very small (Figure 2b). So the di-Gaussian parameterization can be used. In contrast, the radial orbital bound to the He$^+$ ion has only one area of charge localization (Figure 2b) and thus the corresponding DPI amplitude can be represented by just a single Gaussian. This is the first experimental observation of strong modification of the $a_s$, amplitude of a ns-orbital with respect to the one of He.

This modification is related to the structure of the radial wavefunction of the target orbital. In the case of the Cooper minimum, the contributions of the oscillations of the target orbital cancel each other in the real and scalar quantity: the dipole radial integral. In the case of DPI, these contributions add up as complex and angular dependent amplitudes which display an intricate interference pattern. The interference referred to here is similar to that of the electron “two-slit” experiments. Where the wave functions of the electrons, “emitted” from different spatial positions, interfere. Here, similarly, the wave functions of electron pairs “originated” from two different regions of the charge density interfere.

**Figure 2.** (a) The symmetric gerade amplitudes of DPI of Mg at $E_1 = E_2 = 16.4$ eV is shown as a function of the mutual photoelectron angle $\theta_{12}$. The full CCC calculation (red solid line) is fitted with a Gaussian function (blue dashed line) and di-Gaussian parameterization (green dashed line). The Mg amplitude extracted from the experimental TDCS is shown with error bars. (b) The radial orbitals $P(r) = rR(r)$ for Mg $3s$ (red solid line) and He $1s$ (green dashed line).

Original Paper

The Role of the Partner Atom and Resonant Excitation Energy in Interatomic Coulombic Decay in Rare Gas Dimers

In this work experimental evidence for Interatomic Coulombic Decay (ICD) in mixed rare gas dimers following resonant Auger decay is detailed. It is shown that the ICD process can be controlled by the choice of the partner atom in the dimer or of the resonance which triggers the resonant Auger decay.

Interatomic Coulombic Decay (ICD) is a process which occurs when a system containing two or more atoms (or molecules) is perturbed by an event which leaves a singly ionized system with one of its components with an inner valence hole. If the energy of this state lies below the double ionization potential of the isolated atom (molecule), then it cannot decay by autoionization, but only via radiative decay which is a slow process. However, if the atom has a neighbour, the system can relax more quickly by transfer of energy from the excited ion to the neutral partner (via the Coulomb interaction) and the emission of a low energy electron from the latter. This leads to two singly ionized atoms which then undergo a Coulomb explosion. ICD is quite ubiquitous in van der Waals complexes, H-bonded systems, clusters, and condensed phase physics and is considered to be a relevant process in living tissue, where electrons and energetic radical cations may produce irreparable damage to DNA. The result is that the question on how one may control ICD in order to produce low energy electrons and radicals with well-defined characteristics has arisen. A possible route to this goal is to resonantly excite one of the components of the system which then decays to states that either can or cannot undergo ICD for the case of the inner shell resonant excitation of mixed Ar-rare gas dimers. This is illustrated for a mixed Ar-rare gas dimer in the following three step reaction: (1) inner shell excitation, (2) resonant Auger decay and (3) Interatomic Coulombic Decay. The last two of these are illustrated schematically for the Ar₂ dimer in Fig. 1.

\[
\text{Ar} - \text{Rg} + h\nu \rightarrow \text{Ar}(2p_{3/2}^{-1}nl) - \text{Rg} \quad (1) \\
\text{Ar}(2p_{3/2}^{-1}nl) \text{Rg} \rightarrow \text{Ar}^+ - \text{Rg} + e^{-,\text{Auger}} \quad (2) \\
\text{Ar}^+ - \text{Rg} \rightarrow \text{Ar}^+ + \text{Rg} + e^{-,\text{ICD}} \quad (3)
\]

By choosing the resonant photon energy it is possible to “switch on” or “switch off” the ICD channel or indeed “tune” the kinetic energy of the ICD electrons emitted. To demonstrate this effect we have chosen the Ar₂ and NeAr dimers, while the inner shell resonances excited are the Ar 2p⁻¹nl resonance. In a first measurement the Ar⁺-Ar⁺ or Ne⁺-Ar⁺ ion pairs were measured in coincidence with low energy electrons as a function of photon energy, while in the second one the Kinetic Energy (KE) distribution of the low energy electrons produced in coincidence with Ar⁺/Ar⁺ or Ar⁺/Ne⁺ ions were measured in an electron imaging experiment.

Figure 1. Interatomic Coulombic decay in the Ar₂ dimer following resonant inner shell excitation. Reprinted with permission from J. Phys. Chem. Lett. 4 (2013) 1797. Copyright (2013) American Chemical Society.
The measured electron KE distributions for two of the resonances examined are shown in Fig. 2a and 2b. The KE distribution of the ejected electrons increases from the Ar $2p_{3/2}^{-1}3d$ to the Ar $2p_{3/2}^{-1}4d$ resonance (Fig. 2). To rationalize these observations an empirical model based on the assumptions that i) the Ar$^+$ Ar states undergoing ICD can be approximated from an energetic point of view by the corresponding atomic states Ar$^+$ and ii) all states energetically open to ICD actually undergo ICD and therefore the intensity distribution is governed by the probability that the corresponding state is populated by resonant Auger. This simple model does not provide a quantitative description of the process, but, remarkably, it does capture the essence of the problem as shown in Fig. 2. In the second panel of the same figure the comparison between the KE distributions for excitation in Ar-Ar and Ne-Ar dimers is reported. In the Ne-Ar dimers the ICD electrons produced have spectra peaked at 0 eV as confirmed by the model. This occurs because the dissociation limit for the Ar$^+$ Ne$^+$ system lies 5.81 eV above that of Ar$^+$ Ar$^+$ and therefore the electron KE is shifted to lower energies.

In conclusion, it has been demonstrated that ICD represents a major channel in the cascade following core excitation and, equally importantly, that it is possible to tune the ICD electron kinetic energy by choosing the resonance at which the dimer is photoexcited or to switch on or off the ICD channel by exciting the appropriate resonance with the more suitable partner atom.

Figure 2. (a) Ar-Ar dimers: the electron kinetic energy distributions obtained for $\alpha'$Ar$^+$Ar$^+$ coincidences for the Ar $2p_{3/2}^{-1}3d$ to the Ar $2p_{3/2}^{-1}4d$ resonances (left panels) and the ICD electron kinetic energy distributions estimated from experimental RA spectra of the atom (Right panels). (b) Similar to (a) but for the Ar $2p_{3/2}^{-1}3d$ resonance in Ne-Ar and Ar$_2$ dimer, respectively, to illustrate the role of the partner atom in ICD (see text for details). Reprinted with permission from J. Phys. Chem. Lett. 4 (2013) 1797. Copyright (2013) American Chemical Society.

Original Paper
Spatially modulated boron-doped graphene

Here we study the electronic properties of boron-doped graphene by spatially resolved photoemission band mapping on single domain. B-doped graphene films have been grown on copper by chemical vapor deposition using methane and diborane as carbon and boron sources, respectively. A two-step procedure has been optimized to create a doping gradient: as a first step, the surface is seeded with pure graphene islands, while the boron source is activated only in a second stage. The aim of this work is to investigate new strategies for the design of complex graphene architectures with a spatially modulated doping.

Recently, the forefront of the research on graphene has moved from the study of the synthesis and properties of pure films to the investigation of chemically modified systems. The introduction of selected dopants into the honeycomb carbon sp² lattice allows tuning the physical-chemical properties of the prepared materials. Here we report the preparation of boron-doped graphene (B-G) films on copper via chemical vapor deposition, and we provide a detailed microscopic view of the growth mechanism. B-G has been intensively studied theoretically since it is expected to show p-type conductivity representing a crucial material for the development of graphene-based electronics, but it is also important for advanced applications as electrode in photovoltaics and chemical energy storage.

The deposition of B-G layers has been carried out using methane as carbon source and diborane as dopant gas. We chose copper as substrate, because it allows growing single layer films. A two-step route has been carefully optimized and visualized using scanning electron microscopy (SEM): at first, the Cu surface has been exposed to methane and hydrogen for nucleating graphene patches on the surface (Fig. 1a), then diborane was introduced providing boron for doping. Non-stoichiometric boron carbide nanoparticles (CₓBᵧ NPs) are formed competitively on the bare Cu areas between graphene patches (Fig. 1b). We have found that CₓBᵧ NPs can be used as a very effective source of boron, which can migrate by diffusion from the peripheral areas into the graphene islands. Photoemission from the core level has been undertaken to study the chemical structure of the films and to determine the average doping level (1.5 %). Fig. 2a reports the B 1s photoemission line and

Figure 1. SEM micrographs of the CVD growth of B-G with schematic drawings: a) first step of the synthesis showing the formation of large graphene domains covering about 80% of the copper substrates; b) second step with the further growth of graphene islands and the nucleation of some 3D clusters of nonstoichiometric boron carbide on bare copper areas (scale bar 3 µm) (Reprinted with permission from DOI: 10.1021/cm302819b. Copyright 2013 American Chemical Society).
its separation into single peak components. The most significant peak has binding energy (BE) of 189.6 eV, it is associated to sp$^2$ C−B bonds present in graphene, while the components at lower BE can relate to C$_x$B$_y$ particles as observed in the SEM images (Fig. 1b) in between graphene islands. The C 1s photoemission data, reported in Fig. 2b, has main peak at 284.8 eV is related to the C sp$^2$ component of the honeycomb lattice, while the peak at 283.7 eV can be ascribed mainly to substitutional B into the honeycomb lattice, the peak at lowest BE is associated to C$_x$B$_y$ NPs.

To clarify the effect of boron incorporation on the electronic structure of graphene we performed angle-resolved photoelectron spectroscopy (ARPES) measurements at the Spectromicroscopy beamline. The microscopic photon beam allowed to carry out measurements on single graphene domains, while the combined degrees of freedom of sample and analyzer made possible to measure selectively the band dispersion along the Γ−K direction of the first Brillouin zone (Fig. 2c). In Fig. 2d and 2e we report the images of Dirac cones of pure graphene and B−G, respectively. The band structure of B−G is similar to pure graphene with a linear dispersion of the π-band close to the Dirac point, as expected for massless Dirac fermions; one notable difference with respect to pure graphene is the altered position of the Dirac point, which for B-doped layers coincides with the Fermi level.

Theoretically, B−G should be a p-type semiconductor with the Fermi level cutting the Dirac cones below their intersection. This phenomenon is not observed experimentally most probably for the tunneling of electrons from Cu into the empty states introduced by the presence of B. Therefore, the doping operated by the metal contact, which determines n-doping on pure graphene (about 0.3 eV, Fig. 2d), counterbalances the intrinsic p-doping induced by the presence of boron in the graphene lattice, leading to the formation of an almost perfect semimetal (Fig. 2e). This is a quite interesting result showing how the intrinsic properties of the material can be modified by the interaction with the substrate. The present outcome is of paramount importance because it suggests that it would be possible to use this same phenomenon of electronic exchange between metals and doped graphene in order to modulate the electronic structure of supported metal NPs.

Figure 2. a) B 1s and b) C 1s photoemission spectra of B−G, together with the multipeak analysis of the single chemically shifted components. c) The real space structure of a B−G sample, visualized with photoemission microscopy at the K point, darker areas correspond to C$_x$B$_y$ particles, brighter areas are graphene grains (scale bar 10 µm). d) and e) Dispersion of the valence band around the K point for pure graphene and B−G, respectively. Reprinted with permission from DOI: 10.1021/cm302819b. Copyright 2013 American Chemical Society.
Interfacial complexation reactions \textit{in vacuo}: a self-terminating protocol via metal-organic chemical vapor deposition

In the effort to create interfacial coordination complexes with tailored functionality, we report a novel pathway based on metal-organic chemical vapor deposition. As a proof of concept, we studied the reaction of surface confined porphyrins with a ruthenium carbonyl precursor. Synchrotron radiation x ray photoelectron spectroscopy reveals that free-base porphyrin molecules adsorbed on Ag(111) readily undergo metalation with Ru upon exposure to the metal precursor and thermal treatment, with no additional byproducts left on the surface.

The design and engineering of coordination complexes and metal-organic architectures at well-defined interfaces holds great promise in important research areas such as single-site catalysis, light harvesting, and molecular nanomagnetism. Here the ability to incorporate metal centers in unique coordination environments can convey specific functionalities that allow tailoring the physical and chemical properties. Usually, such systems are prepared \textit{in vacuo} either by grafting prefabricated metal-organic complexes on surfaces or by co-deposition of molecular linkers and metal adatoms followed by complexation reactions at the interface. In the case of transition metals such as W, Ru and Ir, the latter method can be severely limited by the high sublimation temperature of these materials, whereas the former relies on the availability of established organic synthesis protocols. This motivated us to investigate an alternative pathway based on metal-organic chemical vapor deposition, which is exemplified in the present work by the reaction of porphyrins with a ruthenium carbonyl precursor, Ru$_3$(CO)$_{12}$, on a Ag(111) surface.
energy signals the incorporation of ruthenium into the macrocycle. Further exposure of this partially metalated film to Ru$_3$(CO)$_{12}$ followed by annealing as before leads to a fully metalated porphyrin layer, as evidenced by a single component in the N 1s spectrum (Fig. 1d). In the specific case addressed here, by combination of quantitative XPS and STM analysis we also found that the reaction proceeds without build-up of surplus material and without any surface byproducts. Interestingly, the 3d$_{5/2}$ photoemission signal from the Ru centers is peaked at a binding energy of 279.6 eV (Figs. 1c,d), which is typical of metallic Ru rather than Ru$^{2+}$ as expected for an isolated Ru porphyrin. This effect in the apparent oxidation state is ascribed to charge transfer from the Ag substrate underneath and further highlights the importance of molecule-substrate hybridization and the resulting novel physical properties of organic monolayers on solid surfaces. In conclusion, this work demonstrates the viability and implementation of a novel approach towards the design of interfacial coordination systems. A simple, reproducible protocol was developed for the on-surface metalation of porphyrins without the need of controlling the molecular coverage and without the build-up of undesirable surface by-products. This represents a versatile, cheap and relatively simple method for implementing and addressing the functionality of a wide variety of metal centers and for the manufacturing of composite materials.

**Figure 1.** Sequential N 1s (left), Ru 3d$_{5/2}$ (middle) x ray photoelectron spectra and corresponding cartoon (right) of the porphyrin Ru metalation process on Ag(111): (a) Monolayer of the porphyrin derivative on Ag(111). (b) Following exposure to saturated coverage of the Ru precursor at 300 K. (c) After annealing to 550 K. (d) After further exposure to saturated coverage of the Ru precursor at 300 K and annealing to 550 K. Adapted with permission from DOI: 10.1021/nn401171z. Copyright 2013 American Chemical Society.
The interest in the O/Ag system arises from its importance in two silver-catalyzed large-scale reactions: the epoxidation of ethylene and the partial oxidation of methanol to give formaldehyde. The O/Ag system has been intensively studied for more than 30 years, but the role played by the different oxygen species on poly- or single crystalline Ag surfaces in the two reactions is still controversially discussed. Our study focused on the preparation of an oxygen species on Ag(111) under UHV (Ultra High Vacuum) conditions that is characterized by an O 1s peak at a binding energy of ~ 530 eV. This oxygen species is of great importance since we could recently show that it is catalytically active during the ethylene epoxidation reaction. The Ag(111) crystal was oxygen loaded by dosing NO\textsubscript{2} at \( T > 470 \) K. NO\textsubscript{2} readily dissociates on Ag(111) into adsorbed oxygen (O\textsubscript{ad}) and NO\textsubscript{ad}. Within a limited temperature range, NO\textsubscript{ad} desorbs and O\textsubscript{ad} remains on the surface. NO\textsubscript{2} was chosen instead of molecular oxygen since an impinging NO\textsubscript{2} molecule gives O\textsubscript{ad} at a 10\textsuperscript{4}-10\textsuperscript{5} higher efficiency than O\textsubscript{2}. Nevertheless, in order to form substantial amounts of the catalytically active oxygen on Ag(111) high NO\textsubscript{2} dosages were required, e.g., at an NO\textsubscript{2} pressure of 10\textsuperscript{7} mbar a dosing time of about 30 h was needed; the corresponding dose is \( \sim 10^7 \) L (Langmuirs), with 1 L = 1.33\times10\textsuperscript{-6} mbar\ s. This explains why it is impossible to prepare this species by dosing O\textsubscript{2} under similar pressure conditions. NO\textsubscript{2} dosing onto Ag(111) at \( T = 495 \) K leads to the formation of an O\textsubscript{ad} phase that is characterized by an O 1s peak at a binding energy of \( \sim 530 \) eV. This oxygen species is of great importance since we could recently show that it is catalytically active during the ethylene epoxidation reaction.

The in situ preparation of a catalytically active oxygen species on Ag(111) and its characterization using the SPELEEM instrument at Elettra are described. Spectroscopically resolved were the O\textsubscript{ad} phase (528.30 eV) and a new oxygen species (O 1s components at 530.20 and 530.75 eV), which occurs after extended oxygen loading. The photoemission peak at 530.75 eV binding energy is attributed to oxygen below the surface. Details on the formation of the catalytically active oxygen species and processes accelerating its accumulation on Ag(111) are discussed.

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for which a total dose of 3300 L NO₂ was used, led to substantial accumulation of the 530 eV oxygen species. The following 6th cycle is displayed in Fig. 1c. Deconvolution of the acquired O 1s spectra shows that the ~530 eV O 1s peak in fact consists of two components, at 530.20 eV (green) and 530.75 eV (blue). The upper panel displays the extracted O 1s peak intensities, converted into coverages. One can see that the intensity of the 530.20 eV component follows the intensity of the 528.30 eV peak, while the 530.75 eV component is anti-correlated. On such surfaces, which were obtained by this cyclic preparation, XPEEM images taken near 530 eV binding energy are uniform, in contrast to the surface obtained under constant NO₂ pressure.

We attribute the O 1s component at 530.75 eV (blue) to oxygen below the surface since its signal intensity is strongly damped by the growing O\text{ad} phase (red) on top of it. This is in line with the fact that the formation of the O\text{ad} phase still appears in LEEM similarly as in the absence of the 530 eV oxygen species (Fig. 1a). The data of Fig. 1c indicate that during de-reconstruction/reconstruction of the Ag(111) surface the rearrangement of the Ag surface atoms helps accumulating the new oxygen species homogenously on the Ag sample:

After completion of the O\text{ad} phase the entire surface is reconstructed and each surface Ag atom has experienced once the structural rearrangement of the surface. As a consequence, on each surface site the probability that the ~530 eV oxygen species forms is the same. One expects a spatially homogenous distribution of this oxygen species, in accordance with the experimental finding. When instead a constant NO₂ is applied the Ag(111) surface permanently remains reconstructed (Fig. 1b), the favorite reconstruction/de-reconstruction process does not occur (which obviously lowers the activation energy), and only low-coordinated sites at steps and step bunches can react. This quite complex result can explain much of the unclear results in the literature about the Ag/O system.

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**Original Paper**

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**Figure 1.** a) Three LEEM images ((0,0)-spot at 19 eV, FOV 15 mm), acquired during growth of the O\text{ad} phase on Ag(111) at T=495 K. The formation of the O\text{ad} phase (imaged dark) was completed after a total NO₂ dose of ~200 L. b) NO₂ dosing at T=480 K at a pressure of (1.0–5.6) 10⁻⁷ mbar onto the completed O\text{ad} phase. After dosing of 5000 and 9000 L a new peak component at ~530 eV appears in the O 1s spectrum. XPEEM imaging (530.3 eV, FOV 10 µm) shows preferential accumulation of the new oxygen species along steps and step bunches. c) Changed NO₂ dosing by inducing the reconstruction/de-reconstruction of the Ag(111) surface at 490 K leads to more efficient accumulation of the ~530 eV oxygen species. After 5 preparation cycles (dosing of 3300 L NO₂) already a substantial amount was accumulated and further enhanced during the displayed 6th cycle (dosing of additional 1000 L).
In the last years the scientific interest on graphene, the two dimensional arrangement of carbon atoms just one atom thick, has grown enormously due to the remarkable properties of this material. In particular, the very high carrier mobility at room temperature, tolerance to high temperature and inertness make graphene the most promising candidate for future nanoelectronics. Several manufacturing methods have been developed to produce graphene layers of various dimensions and quality. However, exfoliation-based techniques produce small flakes or graphene of poor quality whereas large-scale growth on metal substrates requires the transfer of graphene on an insulating support in order to guarantee the conduction through graphene. We have developed a novel transfer-free method to electrically insulate epitaxial graphene from the metal substrate it is grown on. This is achieved by growing an insulating SiO$_2$ layer of the desired thickness directly under the epitaxial graphene layer, through a stepwise reaction between intercalated silicon and oxygen. Firstly, epitaxial graphene is grown on a Ru(0001) crystal surface. The graphene layer is then exposed to silicon that intercalates below graphene and forms a silicide with high-quality, large-area epitaxial graphene can be grown on metal surfaces, but its transport properties cannot be exploited because the electrical conduction is dominated by the substrate. Here we insulate epitaxial graphene on Ru(0001) by a stepwise intercalation of silicon and oxygen, and the eventual formation of a SiO$_2$ layer between the graphene and the metal. We follow the reaction steps by x ray photoemission spectroscopy and demonstrate the electrical insulation using a nanoscale multipoint probe technique.

![Graphene formation and Si evaporation on Ru(0001): XPS of the C 1s and Ru 3d core levels.](image)

(a) Core level spectra measured on the clean Ru(0001). The components S, B' and B correspond to first layer, second layer and bulk Ru atoms, respectively. (b) GR on Ru(0001) shows two C 1s peaks for carbon strongly (C2) and weakly (C1) interacting with the Ru surface. A C-induced component appears in the Ru core level, marked as S'. (c) Intercalation of Si that alloys with the metal forming Ru silicide, giving rise to two Ru 3d$_{5/2}$ peaks (Ru1 and Ru2) and a single C 1s peak C1. The central inset displays a 2D plot of the fast XPS spectra measured while evaporating Si on GR, showing the decay of C2 and the rise of the C1 component. Reprinted with permission from DOI:10.1021/nl301614j. Copyright 2012 American Chemical Society.
the metal. Finally, by exposure of
the surface to molecular oxygen,
the metal silicide is oxidized to
form an insulating SiO$_2$ layer that
separates graphene from the
metal. We have also shown that
in this system the transport is
dominated by graphene and not by
the underlying metal by performing
lateral transport measurements.
All the processes taking
place under the graphene
layer have been followed by
high-energy-resolution x ray
photoelectron spectroscopy
(XPS) experiments performed at
the SuperESCA beamline. The
starting point is the clean Ru(0001)
surface (Fig. 1a). After graphene
growth, the C 1s spectrum
shows two contributions from
graphene regions weakly (C1)
and strongly (C2) interacting with
the Ru substrate. The subsequent
exposure to silicon at 720 K causes
the complete conversion of the
C2 component into the narrow
component C1 (Fig. 1c). At this
point, as shown in Fig. 2, the
Si 2p spectrum exhibits two doublet
components, Si1 and Si2, likely
due to the formation of Ru silicide
(Fig. 1b). The surface is then
exposed to molecular oxygen at a
temperature of 640 K. The oxygen
intercalates below graphene,
leading to the progressive silicide
oxidation, as evidenced by the
evolution of the Si 2p spectrum
which transforms into a broad
peak at ~103 eV, indicative of Si
in a SiO$_2$ environment. The C 1s
intensity converts into the single
and narrow C3 peak, interpreted
as graphene supported on SiO$_2$.
The transport measurements
show that the recorded resistance
has a behavior typical of a two
dimensional system and its
absolute value has the expected
order of magnitude for weakly
doped graphene (~1000 $\Omega$)
which is five orders of magnitude
higher than that expected for the
clean ruthenium surface. The
demonstrated process combines
the advantages of high-quality
large-scale graphene growth with
a non-conducting substrate. These
results are expected to provide
new insight for fundamental
studies on graphene, and to
open new perspectives for the
advancement of next-generation
graphene-based devices.

Figure 2. Oxidation of the Si intercalated graphene/Ru(0001) interface following O 1s,
C 1s, and Si 2p core level spectra. Before oxidation the bottom Si 2p spectrum shows
two doublets Si1 and Si2 due to Ru-Si bonds in the silicide phase. During oxidation
the silicide decomposes and oxygen binds exclusively to Si forming SiO$_2$ as witnessed by
the development of the Si 2p and O 1s core level spectra. Reprinted with permission from
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Ionic liquids are molten salts that are liquid below 100 °C. They consist of an organic cation, and an organic or inorganic anion. Their physico-chemical properties can therefore be “tuned” using appropriate ions and ligands. Furthermore, they intrinsically exhibit unusual properties, such as an extremely low vapor pressure. ILs (Ionic Liquids) have thus recently stimulated the development of new concepts and applications in catalysis, lubrication, solar cells, and molecular electronics. These applications have in common the use of a thin IL layer spread onto oxide supports but the interfacial chemistry of such systems remains largely unexplored.

Our experiments aim at better understanding what kind of interactions occur between different oxide supports and ILs. We have performed HR-PES (High Resolution PhotoElectron Spectroscopy) and RPES (Resonant PhotoEmission Spectroscopy) measurements of the ionic liquid \([\text{C}_6\text{C}_1\text{Im}]\text{Tf}_2\text{N}\) deposited in situ on clean and ordered CeO\(_2\)(111), and partially reduced CeO\(_2\)-x. Both films were prepared on Cu(111) (Fig. 1). HR-PES allows discrimination between the elements constituting the IL (C in different chemical environments, N, F, S, and O). In particular, the anionic and cationic C signals are very well separated (Fig. 2). RPES allows a precise determination of the Ce\(^{3+}/\text{Ce}^{4+}\) ratio, thus providing complementary information about the reduction state of the surface. Such experiments are only possible with synchrotron sources and on a limited variety of surfaces. With the combination of both techniques, however, we were able to simultaneously and quantitatively follow the chemical transformations within the IL film and within the substrate as the temperature of the system was increased stepwise from 160 to over 600 K.

Starting with the partially reduced surface (Fig. 2b), modifications in the anionic region of the HR-PES spectra were observed concurrently with further reduction and then re-oxidation of the substrate. This indicated that the anion reacted with this surface following a redox pathway. Interestingly, the cation seemed to continuously desorb from the surface over the temperature range investigated, without observable reaction. Conversely, with the fully oxidized surface (Fig. 2a), we observed important changes in the cationic component of the IL first, followed by changes in its anionic part. The oxidation state of the surface, however, remained mostly constant throughout the experiment, which
thus indicated that the chemical reactions observed must be of the acid-base type. We also identified the presence of strongly bound organic surface species stable well above the desorption temperature of the pure IL. We propose that they could derive from \( N \)-heterocyclic carbenes neighboring alkoxy species.

In another series of experiments, we investigated the adsorption of 5-oxo-[C\(_5\)C\(_1\)Im][Tf\(_2\)N] on the same surfaces, that is, a similar IL with a carboxyl (C=O) group attached to the alkyl chain of the IL. We found that such functionalization changes the orientation of the ionic liquid at the surface as the carboxyl group pulls the alkyl chain toward the surface. We also found that the functionalization does not change the chemistry of the IL very much upon heating.

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High quality and large area graphene (GR) layers can be synthesized by epitaxial growth on transition metals surfaces. However, the interaction with the substrate is the major drawback of this technique because it prevents the typical electronic properties from being established. On the other hand, a weak coupling leads to poor crystalline order and to the formation of GR domains. It is thus difficult to achieve at the same time a weak interaction with high structural quality. A possible solution to this dilemma is the epitaxial growth on a metal substrate which provides a sufficiently strong interaction with GR and the subsequent decoupling by intercalation of atomic or molecular species. Oxygen intercalation appears as a viable route to decouple GR/metal interfaces, but so far it has been demonstrated only for incomplete monolayers or islands. Our work proves that oxygen intercalation is possible for a complete GR layer on Ir(111). By combining XPS (X ray Photoelectron Spectroscopy) measurements, performed at the SuperESCA beamline of Elettra and ARPES (Angle Resolved Photoelectron Spectroscopy) performed at SGM-3 beamline of ASTRID, Denmark, we demonstrate that molecular oxygen intercalation leads to an intact quasi free-standing Gr layer with the disappearance of the characteristic moiré-induced features in the electronic band structure due to the interaction with the substrate.

Figure 1. (a) C 1s core level spectra after different intercalation steps of oxygen under GR/Ir(111). In each step oxygen was dosed at a pressure of 5x10^-3 mbar for 10 min and at a sample temperature from 430 to 520 K. (b) BE shift of the C 1s peak maximum as a function of the oxygen dose. (c) Band dispersion along a line orthogonal to the Γ-K direction for GR/Ir(111) and (d) after oxygen intercalation. Reprinted with permission from DOI:10.1021/nn302729j. Copyright 2012 American Chemical Society.
intercalation conditions we dosed molecular oxygen on GR grown on Ir(111) at different substrate temperatures (Fig. 1a). The C 1s spectrum measured on the as-grown GR shows a single, narrow peak at a binding energy (BE) of 284.14 eV. Up to 470 K, oxygen exposure causes merely the appearance of weak features due to the formation of C-O bonds in GR/Ir(111) (284.4 and 285.2 eV) and a broad peak at 284 eV stemming from inhomogeneous perturbation of the C-Ir interaction, caused by the effective penetration below GR of some O$_2$ molecules that dissociatively chemisorb on the Ir surface. A complete intercalation is achieved at 520 K, leading to a narrow C 1s spectrum peaked at 283.60 eV. At this point the GR layer is “lifted” from the Ir surface; that is, it is decoupled from the Ir(111) through the adsorbed oxygen layer. The same intensity of the C 1s spectrum measured on the as-grown and on the O-intercalated GR excludes that C atoms are etched during the exposure to O$_2$. The relation between the C 1s BE shift and the amount of intercalated oxygen is shown in Fig. 1b. Most of the C 1s BE shift is induced in the first part of the intercalation: a coverage of $\sim$0.4 ML induces a C1s shift of -0.44 eV, whereas the subsequent increase to $\sim$0.6 ML determines only an additional shift of -0.1 eV. This C 1s BE shift is attributed to charge transfer from GR to the oxygen-covered metal surface, leading to hole-doped GR. The behavior of the C 1s peak is paralleled by that of the valence band dispersion. Pristine GR/Ir(111) shows a linearly dispersing π-band characterized by weak replicas and minigaps (Fig. 1c), fingerprints of the GR-substrate interaction, which disappear after oxygen intercalation (Fig. 1d). The Dirac point shifts by about 0.57 eV towards lower BEs, because of the hole doping. The thermal stability of the O-intercalated GR/Ir(111) interface is explored by following the C 1s core level spectrum during sample annealing to about 700 K (Fig. 2a). The carbon peak is quite stable up to 570 K and suddenly undergoes a rapid transition recovering the BE position and the line shape characteristic of the GR/Ir(111) surface, probing oxygen deintercalation. The C 1s intensity decreases by $\sim$18%, implying that such an amount of C atoms has been lost in the deintercalation process. Additional intercalation/deintercalation cycles readily occur at lower oxygen pressure and temperature, consistently with an increasingly defective lattice.

In conclusion, our findings demonstrate that oxygen intercalation is an efficient method to fully decouple an extended layer of GR from the metal substrate it is grown on, paving the way for fundamental research on GR, where extended, ordered layers of free-standing GR are of utmost importance.

**Original Paper**

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![Image of Figure 2](https://example.com/image.png)

**Figure 2.** (a) C 1s thermal evolution on GR/O/Ir(111) during the temperature ramp from 320 to 690 K at 0.5 K/s. The top and bottom spectra are before and after annealing, respectively, while the central panel represents the C 1s intensity plot during sample heating. (b) C 1s intensity and BE shift vs temperature obtained from the spectra in (a). The inset shows the BE first derivative. Reprinted with permission from DOI:10.1021/nn302729j. Copyright 2012. American Chemical Society.
Rippling and bonding of a graphene superlattice on Ir(100)

The complex interaction between graphene and a support with non-threefold symmetry may result in a peculiar film morphology and structure. On the square Ir(100) we discovered flat and buckled graphene phases that coexist at room temperature; they form stripe-shaped domains which relieve the strain accumulated after cooling the film below growth temperature. In the buckled phase, a small fraction of the carbon atoms chemisorbs to the substrate, originating a textured structure with exceptionally large one-dimensional ripples of nm periodicity. The two graphene phases exhibit distinctively different electronic structure.

Graphene on Ir(100), a square symmetry support, provides a remarkable model for investigating the intriguing physics of the metal-graphene interface. In our study on this system, we unraveled the interplay between film and support, disentangling the effects of the film configuration and substrate interaction on the quasi-particle dispersion. In order to overcome the challenges imposed by the complex structure of this interface, we employed advanced experimental and theoretical methods. Spectroscopic photoemission and low energy electron microscopy (SPELEEM) measurements were carried out at the Nanospectroscopy beamline of Elettra, and were complemented by scanning tunneling microscopy (STM) for characterization at the atomic scale. The experimental results were corroborated by density functional theory (DFT) calculations.

STM data show that these two regions correspond to graphene phases characterized by buckled (BG) and flat (FG) morphology, respectively, with the buckled phase exhibiting perfectly regular stripes separated by 2.1 nm. The graphene honeycomb lattice is continuous across the stripes and passing from flat to buckled regions, see Fig. 1e-g. The unit cell of the buckled phase was identified by STM and microprobe low energy electron diffraction. The equilibrium atomic positions were determined theoretically (see Fig. 1h and i). By using the DFT-D approach, taking into account Van der Waals interactions, the minimum and maximum separation between graphene and Ir were found to be 2.1 Å and 3.8 Å, respectively. The buckling of 1.7 Å is significantly larger than those previously found for chemisorbed graphene. The analysis of the calculated spatial distribution of the charge density, used to generate the image in Fig. 1h, indicates that only 11%...
of the C atoms are chemisorbed to iridium. By imaging emission from graphene's π-band at the reciprocal space K point, photoemission microscopy enabled a direct comparison of the local density of states (DOS) of flat and buckled graphene. The low intensity observed in the latter suggests the disruption of the Dirac cones (see Fig. 2). In this regard, theory revealed that the metallic-like character of the buckled phase does not originate from strain or rippling, but rather from the chemisorption to the substrate. The novelty highlighted in our study is that the change in the graphene DOS at the Dirac point is due to the chemisorption of just a small fraction of the atoms in the unit cell. Another striking feature is that the buckled phase can be reversibly transformed in the physisorbed phase by varying the sample temperature. This observation suggests that the film changes morphology and structure in order to relieve the strain resulting from the different thermal contraction of the substrate and the anchored graphene island. At variance with the case of Ir(111), where narrow and tall wrinkles are formed, here graphene organizes in microscopically extended domains. Regions of flat unstrained, physisorbed graphene alternate with the denser, buckled phase. The relative proportion of the two phases is dictated by their density difference and the thermal contraction of the substrate upon cooling below growth temperature. Further, the domain orientation of the buckled phase, about 70° with respect to the substrate main direction, is determined by the anisotropic difference in density between BG and FG. We expect that regular one-dimensional ripples might be observed in a multitude of sp²-bonded layers supported on square or rectangular symmetry surfaces. We also highlight the potential of buckled graphene as a template for synthesizing one-dimensional supported nanostructures characterized by fascinating physical and chemical properties.

Figure 2. a) microprobe-ARPES pattern of graphene/Ir(100) at room temperature; (b) cross section through one of the Dirac cones along a plane normal to Γ-K, as indicated in (a); (c) the intensity profile along the vertical red line in (b) shows the Fermi level (d) dark-field XPEEM image at the K point at the Fermi energy; the image intensity is proportional to the local DOS; (e) normal emission XPEEM image at Γ. Reprinted with permission from DOI:10.1021/nn402178u. Copyright (2013) American Chemical Society.
Organic chiral molecules are adsorbed on metallic substrates to obtain chiral surfaces transferring the chirality from the molecules to the surface: this process is driven by the availability of hydrogen atoms. We report, by combination of core level and valence band PES (Photoelectron Spectroscopy), LEED (Low Energy Electron Diffraction) and DFT (Density Functional Theory) calculations, on the adsorption of the d-enantiomer of alaninol on Cu(100) and on Cu(110) surfaces, revealing dehydrogenation at different substituent groups depending on the coverage and on the substrate symmetry.

Functionalized metal surfaces with chiral molecules to obtain two-dimensional (2D) chiral surfaces are of wide interest for biological processes and biomedicine and of fundamental importance in enantiomeric compound separation, catalysis and sensors. Chirality is transferred from molecules to the surface via the formation of self-assembled monolayers, driven by supramolecular effects as long-range interactions and hydrogen bonds.

H-bonding involving alcoholic and/or amino groups plays a central role in guiding a specific chiral self-assembled structure: the number and position of the hydrogen atoms is relevant for the degree of surface enantioselectivity and possible dehydrogenation due to the adsorption should be considered. Here DFT evaluation of CLSs (Core Level Shifts) and VB (Valence Band) DOS (Density Of States) allows to address the experimental features observed in the photoelectron experiments. From the inspection of XPS (X-ray Photoelectron Spectroscopy) spectra obtained depositing d-alaninol on Cu(110) and on Cu(100), different interactions with the surface can be detected as a function of the substrate symmetry and molecular coverage (Figure 1). At LC (Low Coverage) the BEs (Binding Energies) of O 1s and N 1s present the same values on the two surfaces showing that, when inter-molecular interactions are negligible, d-alaninol interacts with the substrate in a similar way. Calculations show that the most stable adsorption geometry at LC is an O-dehydrogenated structure.
on both surfaces. The O 1s signal at 530.7 eV corresponds to this chemical situation, while the N 1s signal at 399.7 eV is due to intact amino groups, consistently with LT (Low Temperature) measurements.

At SC (Saturated Coverage), where the self-assembled structure is present at the surfaces, intermolecular interactions become stronger. Additional peaks are detected at SC: on Cu(110) the new O 1s peak at 532.4 eV is attributed to intact hydroxyl groups (in agreement with LT experiments and with the calculated CLSs for molecules with an intact or dehydrogenated hydroxyl group). The second N 1s peak arising at SC on Cu(100) at 397.5 eV is attributed to dehydrogenated amino groups, being its BE shift from the most intense peak in fair agreement with the calculated CLSs.

PES measurements at the VB are interpreted with the help of total and partial DOS calculations. Figure 2 reports the VB of d-alaninol adsorbed on Cu(110) (b) and Cu(100) (c) surfaces at LC and SC, along with the valence spectrum obtained for d-alaninol in gas phase (Figure 2a). The VB spectra at SC for both Cu(110) and Cu(100) surfaces show several structures (present also at LC with lower intensity), labeled from A to F, not present in the valence band of clean copper. The higher BE features (from C to F), can be one-to-one correlated with those in the gas phase spectrum and are attributed, on the basis of calculations, to electronic molecular orbitals delocalized on the whole molecule.

Two additional structures, appear in the valence band at 1.7 eV (A) and 4.3 eV (B) both for Cu(110) and Cu(100): being attributed to bonding (B) and antibonding (A) states, they are the fingerprints of alaninol chemisorption on the copper surfaces. Calculations show that at LC on both surfaces these structures are related to O 2p states involved in the molecule-substrate bonding (labeled as A', B', A'', B'' in Figures 2d and 2f). At SC, on Cu(110) (Figure 2e) part of the molecules are intact and do not show significant energy contribution at A', while on Cu(100) (Figure 2g) A'' presents also contribution from N 2p states, witnessing the dehydrogenation of the amino group, as a confirmation of the XPS results. In conclusion, combining PES with DFT calculations, important features of the adsorption of d-alaninol on Cu(110) and Cu(100) have been pointed out. The dehydrogenation process occurs following different pathways on the two surfaces and is driven by the interplay between supramolecular interactions and substrate symmetry.

Figure 2. Left panel: experimental VB spectra obtained at RT (hν=50 eV, Γ point) for d-alaninol in gas phase (a) and d-alaninol adsorbed on Cu(110) (b) and on Cu(100) (c) for LC and SC. Right panel: computed total DOS and PDOS of 2p orbitals for C, N and O for d-alaninol on Cu(110) (d) O-dehydro geometry; (e) intact geometry and Cu(100) (f) O-dehydro geometry; (g) O- and N-dehydro geometry). A broadening of 0.27 eV has been applied. Peaks are labeled to make a correspondence with the experimental structures. Reprinted with permission from DOI:10.1021/jp401822h. Copyright 2013 American Chemical Society.

Original Paper
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Quantifying Through-Space Charge Transfer Dynamics in π-Coupled Molecular Systems

With resonant photoemission and Core-Hole-Clock method we determine ultrafast delocalization of excited electrons between π-stacked aromatic rings in [2,2] paracyclophane (22PCP) and [4,4]paracyclophane (44PCP) molecules adsorbed on Au(111). Charge transfer in 22PCP with 0.3 nm inter-ring separation occurs in 2 fs compared to 50 fs in 44PCP, where rings are 0.4 nm apart. We relate this slower dynamics to the weaker inter-ring coupling and reduced conjugation of empty orbitals between the 44PCPC rings.

In this work, we probe the relation between Charge Transfer (CT) dynamics and π coupling in aromatic systems by comparing two molecules, [2,2]paracyclophane (22PCP) and [4,4]paracyclophane (44PCP) adsorbed on Au(111). 22PCP and 44PCP (Fig. 1) can be represented as two aromatic rings joined together as eclipsed ‘bilayers’ using a scaffold of two or four aliphatic carbon chains respectively. 22PCP is a strained system with an average inter-ring distance of 3 Å, while 44PCP has an inter-ring separation of 4 Å. By comparing these two systems with well-defined, but dissimilar inter-ring distances, we are able to study the effect of inter-ring coupling on through-space charge transport in π-stacked systems. X ray Photoemission Spectroscopy (XPS), Near-Edge X ray Absorption Fine Structure (NEXAFS), and first-principles Density Function Theory (DFT) calculations were employed to establish that both molecular systems, 22PCP/Au(111) and 44PCP/Au(111), have similar adsorption configurations, molecule-metal adsorption energies and molecule-metal adsorption distances.

Figs. 1a and 1b show XPS spectra for monolayer and multilayer films of 22PCP and 44PCP. The C 1s peaks for both molecules display similarly broad and asymmetric shapes due to initial state differences between the sp² C and sp³ C atoms. Both monolayers show the same screening-induced shift to lower binding energy by 0.4 eV relative to the multilayer phase. C K-edge NEXAFS measurements on 22PCP (44PCP) are reported in Figs. 1c (1d). We determine an average tilt angle (47º ± 5º for 22PCP and 45º ± 5º for 44PCP) for the PCP rings with respect to the surface by comparing the ratio of NEXAFS intensities with incident electric field perpendicular (p-pol) and parallel (s-pol) to the sample. This evidences similar adsorption geometry for both molecular monolayers.
To determine dynamics of charge delocalization between π-stacked rings in 44PCP and 22PCP molecules we use the CHC method implemented within the Resonant Photo Electron Spectroscopy (RPES) experiment. We compare the resonant intensities of PCP monolayers coupled to the Au substrate \( I_{\text{coupled}} \) to those of the PCP multilayers \( I_{\text{isolated}} \) and determine CT time as

\[
\tau_{\text{CT}} = \tau_{\text{CH}} \frac{I_{\text{coupled}}}{I_{\text{isolated}} - I_{\text{coupled}}}
\]

with \( \tau_{\text{CH}} = 6 \) fs being the C 1s core-hole lifetime. This method relies on measuring the core-hole decay channels in which the excited electron is transferred to the substrate, and provides information on the sub-femtosecond CT dynamics. Fig. 2 shows RPES maps of the participator decay across the C1s->LUMO resonance for multilayer and monolayer films of 44PCP and 22PCP. Non-resonant photoemission and normal Auger emission have been subtracted. By quantifying the signal intensity \( I \) in these maps we obtain an average CT time for each molecular monolayer, \( \tau_{44} = 1.4 \pm 0.5 \) fs and \( \tau_{22} = 6.0 \pm 0.6 \) fs, for 22PCP and 44PCP respectively. To further quantify this analysis, we develop a one-parameter model for CT times from top and bottom rings of both monolayers to the substrate. We assume that i) CT times from the bottom rings (closer to Au) for both 22PCP and 44PCP monolayers are equivalent, and ii) CT times from the bottom rings are at least as fast as those from the top rings. With this, we find that \( \tau_{\text{isom}} = 0.7 \pm 0.3 \) fs while that from the top rings are \( \tau_{44}^{\text{top}} = 2.3 \pm 0.6 \) fs and \( \tau_{22}^{\text{top}} \geq 50 \) fs, for the 22PCP and 44PCP, respectively. CT between aromatic rings 4 Å apart is therefore 20 times slower than that between the rings 3 Å apart. In conclusion, we find that despite their very similar interaction with Au(111), the quenching of RPES intensity is stronger in monolayers of 22PCP than in those of 44PCP, indicating a much faster electron delocalization between rings with reduced inter-ring separation. We find that the CT time across the π-system of 22PCP is about 1-2 fs and about 20 times faster than across that of 44PCP. We attribute this shorter CT time to the higher conjugation of the LUMO* orbital in the presence of a localized core-hole (see DFT calculated orbitals in Fig. 2c and 2d). CHC measurements therefore allow us to quantitatively probe the relation between π-π coupling and CT dynamics.

Figure 2. a,b) RPES maps of the participator decay across the C1s->LUMO resonance for multilayer films of 22PCP and 44PCP. c,d) RPES from monolayer films of both molecules. The intensity of c compared to a is much lower than that of d to b, indicating fast charge transfer in 22PCP. e, f) DFT calculated lowest unoccupied orbitals for 22PCP (left) and 44PCP (right) in the presence of a core-hole (core-hole position indicated in yellow). The renormalized unoccupied orbitals have very different spatial distributions, which impacts CT times. Reprinted with permission from DOI:10.1038/ncomms2083.
Massively Parallel Multilayer Thick Silicene Nanoribbons

Massively parallel, multilayer thick, silicene nanoribbons (SiNRs) have been synthesized on Ag(110) surfaces. These perfectly aligned SiNRs show cone-like dispersion of their $\pi$ and $\pi^*$ bands in angle-resolved photoemission at both ends of their one dimensional (1D) Brillouin zone (BZ), demonstrating the presence of massless Dirac fermions in the vicinity of the Fermi level. This confers to these graphite-like silicon nanostructures composed of stacks of silicene unique electronic properties opening promising perspectives for future nanometric devices.

Silicene, a one-atom thin silicon sheet arranged in a honeycomb lattice similar to graphene, does not exist in nature, but it has been synthesized on a few metallic substrates, i.e., on epitaxial zirconium diboride thin films grown on silicon (111), on iridium (111), and, especially, silver (111) single crystal surfaces. Then multilayer silicene has been observed in real space by scanning tunnelling microscopy (STM) and further characterized by scanning tunnelling spectroscopy (STS) as well as angle resolved photoemission spectroscopy (ARPES).

Fig. 1 displays high-resolution STM images of multilayer-thick SiNRs grown at ~470K on the Ag(110) surface. These massively parallel SiNRs are all aligned along the [1-10] direction of this anisotropic silver surface. Each SiNR appears as a regular stack of silicene layers with a pyramidal cross section and a very high aspect ratio. The lengths can reach more than several hundred nanometers, while widths and heights vary between 10×30 nm and 2×5 nm; the successive steps height are $h \sim 0.3$ nm. The growth behavior of Si deposited on the Ag(110) surface (at about 470K) was derived by plotting the silicon LVV and silver MNN Auger transitions as a function of the silicon deposition time at constant flux. Their respective increase and decay have revealed directly a Stranski-Krastanov growth mode. A clear break, after initial linear variations points to the completion of a kind of wetting layer composed of perfectly aligned, atom-thin, ~1.6 nm in width (4 $a_{Ag-Ag}$ nearest neighbor distances along the Ag [001] direction), silicon nanoribbons.

Figure 1. (a) STM 3D view of a single SiNR on Ag(110) (30 × 20 nm$^2$; $V = 0.2$ V; $I = 0.1$ nA); (b) STM image of an ensemble of such multilayer-thick SiNRs (400 × 400 nm$^2$; $V = -0.6$ V; $I = 1$ nA); (c) Corresponding RHEED pattern, showing the x4 periodicity (the large arrows indicate the Ag(110) integer streaks and the small ones the 1/4 order streaks; (c) P1 line profile along the [100] Ag direction. The dashed ovals, marked both on top and at the bottom side of the multilayer SiNR evidence the x4 symmetry. Adapted from P. De Padova et al., Nano Lett. 12, 5500 (2012).
forming a highly perfect 4×5 grating with a pitch of just ~2 nm, which nominally covers only 80% of the Ag(110) surface because of their a\textsubscript{Ag-Ag} separation. Beyond the break, 3 dimensional growth of the long Si nanostructures takes place. The corresponding RHEED patterns show a x4 reconstruction related to epitaxial silicene along the [1-10] Ag direction.

Fig. 2. displays ARPES measurements taken along the lengths of the SiNRs, the [-110] direction, i.e., the E(k\textsubscript{||}) band dispersions along the \( \Gamma \rightarrow \bar{X} \) direction that would correspond to the \( \Gamma \rightarrow K \) one for 2D silicene). Assuming a honeycomb silicene lattice for each layer within the stacks (the step height of about 0.3 nm between successive layers, similar to that anticipated for graphite-like silicon, supporting this assumption), the 1.08 Å\(^{-1} \) value for the wave vector at the Dirac point yields a projected Si-Si nearest neighbour distance within the hexagons of ~2.24 Å, in excellent accord with DFT simulations.

The geometry of these multilayer-thick epitaxial SiNRs results from that of their atom-thin precursors within the 4×5 grating. Specifically, they are zigzag silicene nanoribbons with hexagon apexes aligned along their lengths, where a quasi perfect match exists: 4 Ag-Ag basis vectors along the [-110] direction coinciding with 3 silicene basis vectors. This geometry reflects the x4 symmetry found in real space STM images as observed in both low energy and reflection high energy electron diffraction (LEED/ RHEED patterns). Furthermore, this x4 periodicity along the SiNRs zigzags corresponds with that obtained on epitaxial silicon sheets showing a 3×3 super cell in coincidence with a 4×4 silver cell on Ag(111) surfaces. Clearly the 3:4 matching ratio governs the parallel epitaxial orientation in these two 1D and 2D different situations.

For these multilayer-thick SiNRs we derive a very high Fermi velocity of \( \sim 1.3 \times 10^6 \) ms\(^{-1} \), about five time larger than that found previously for the atom-thin ones within the 4×5 first layer grating. It can be compared favourably with that reported for free standing graphene (1.1×10\(^6\) ms\(^{-1}\)) or graphite (1.0×10\(^6\) ms\(^{-1}\)).

The exceptional electronic properties of such silicene-based, multilayer thick, massively parallel, one-dimensional silicon nanostructures opens promising perspectives for potential applications, provided a convenient way to remove them from their metallic silver substrate is found.

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Molecular self-organisation is a viable strategy for producing new nanoscale devices. By combining experimental results and density functional theory calculations we studied the self-assembling of ordered molecular chains of Fe–phthalocyanines on Au(110). This molecular architecture results from a surface self-templating effect, yielding a molecular-induced reconstruction of the Au surface and the rehybridization of the molecular electronic states localized on the metallic center. These effects are explained on the basis of surface thermodynamics and symmetry breaking of the molecular states.

The ability of molecules to autonomously organise into well-defined architectures has the potential to be exploited to produce electronic devices at the nanometer scale. For instance, metallorganic molecules can form regular patterns on several surfaces and are capable of exposing regular arrays of coordinated metallic ions. Since coordinated metals can absorb visible light, catalyze chemical reactions, and act as single-atom magnets they are ideal candidates for catalytic and data-storage devices, as their functioning is based upon both structural and electronic properties of the overall system. In this framework, metal-phthalocyanines (Fig.1 blue fourfold molecule on the right) are of particular interest as they have a variety of optical and magnetic properties that can be tuned by substituting either the coordinated metal or the underlying surface. For these characteristics, phthalocyanine molecules are widely used as dyes in the textile industry and in recordable compact disks, and have a wide range of potential applications as single-molecule component for the fabrication of (molecular) transistors, miniaturised data storage devices, dye sensitised solar cells, and organic solar cells. Our work focused on the interaction between iron-phthalocyanine (FePc) molecules and the Au(110) surface. We showed how the Au(110) nanostructured surface can strongly affect the self-organised molecular overlayer, demonstrating the strong templating effect on the obtained supramolecular structure, explaining why the surface structure reconstructs upon molecular deposition and correlating the system electronic and spectroscopic properties to these structural modifications. While the clean Au(110) surface is known to naturally reconstruct with a (1 x 2) periodicity, we showed by scanning tunneling microscopy (Fig.1, centre) that the FePc molecular adsorption on the same Au(110) surface promotes a local (1 x 5) reconstruction which, in turn, drives the assembly of molecular chains along its orthogonal direction. By low energy electron diffraction (Fig.1, left) we showed that the periodicity of the molecular assemblies is incommensurate to the surface periodicity along the nanorods direction.}

**Figure 1.** (left) LEED image (centre) STM topography (right) molecular model of adsorption and surface reconstruction. Adapted with permission from DOI:10.1021/jp211036m. Copyright 2012 American Chemical Society.
the chain, while density functional theory calculations revealed the thermodynamic origins of the molecule-driven substrate reconstruction as well as its lowest energy configuration (Fig.1, right). We showed that the energy cost to reconstruct the surface into a more suitable template is largely compensated by the larger FePc adsorption energy. As it is the FePc itself to drive the surface reconstruction of its supporting surface to enhance the mutual binding, we called this “self-templatting.” The FePc/Au(110) interaction also induces a rehybridization of the electronic states localized on the central metal atom breaking the molecular 4-fold symmetry. By photoemission and absorption spectroscopy exploiting light polarization (Fig.2, left) we showed how the molecular adsorption is controlled by a symmetry-determined mixing between the electronic states of the Fe metal center and of the Au substrate. By comparing the dichroic response of the photoemission and absorption data with the electronic density of states predicted by the DFT calculations (Fig.2, left) we showed how the electronic structure of the surface-adsorbed FePc molecule presents a number of states that preserve their molecular nature and that can be directly correlated to those of the isolated molecule. A strong FePc/surface interaction is highlighted by the complete hybridization of the Fe d\(z^2\) molecular orbital with the d\(z^2\) orbital of the Au atom directly underneath the Fe center. This effect is particularly enhanced around the Fermi level, but it affects all the Fe electronic states with \(z\) component. The agreement of the calculated electronic structure with the main experimental spectral features, allows us to clarify that these states are associated to a distorted molecular structure displaying a trigonal bipyramidal geometry of the ligands around the metal center with the surface chemically acting as a fifth ligand.

Figure 2. (left) photoemission spectra of the valence band close to the Fermi level for a single-layer of FePc on Au(110), (right) DFT calculated molecular state close to Fermi level. Adapted with permission from DOI:10.1021/jp300663t. Copyright 2012 American Chemical Society.

Original Paper


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High-resolution x-ray spectroscopy and density functional theory calculations show that 2H-tetraphenyl-porphyrins metalate at room temperature by incorporating a surface metal atom when a (sub)monolayer is deposited on 3d magnetic substrates, such as Fe(110) and Ni(111). The calculations demonstrate that the redox metalation reaction would be exothermic when occurring on a Ni(111) substrate with an energy gain of 0.89 eV upon embedding a Ni adatom in the macrocycle.

The possibility to obtain systems where the magnetic or catalytic atoms are well separated and arranged in regular arrays is allowed at the nanoscale by using molecular self-assembly of π-conjugated molecules containing metal ions. Porphyrins, ubiquitous in many aspects of nature, are a class of π-conjugated molecules with a planar macrocycle that can accept metal ions of different kind at the center (metalation), thus forming metallo-porphyrins. As such, synthetic and naturally occurring metallo-porphyrins have been used extensively due to their catalytic, photophysical and magnetic properties as biomimetic agents in several aspects of technology. Man-made metallo-porphyrin units self-assembled into complex and functional superstructures are, therefore, exploding in recent years. There are several ways to metalize porphyrins by wet-chemistry, but even more interesting is, instead, the metalation of porphyrins in Ultra High Vacuum (UHV) by metal evaporation onto 2H-porphyrin self-assembled on surfaces. This method allows obtaining metallo-porphyrins that, typically, are not stable as single molecules thanks to the action of the support surface, which stabilizes the valence state of the evaporated metal. A risk, however, is the formation of metal clusters in addition to metallo-porphyrins due to the reduced mobility of some metal ad-atoms or to an excessive metal ion deposition.

Following seminal studies on Cu surfaces, we generalize an alternative route to porphyrin metalation in UHV without the need of ion evaporation and post-growth annealing. Using synchrotron radiation spectroscopy we demonstrate that depositing at room temperature one
monolayer of 2H-Tetraphenyl-Porphyrins (2H-TPP) on Fe and Ni substrates, a substrate ad-atom binds directly to the macrocycle and metalates the porphyrins. For these molecules core level photoemission is a very sensitive tool of metalation. Actually, in the free-base macrocycle two different nitrogen atoms are present, iminic nitrogen (-N-H) and pyrrolic nitrogen (=N), with a quite different N 1s binding energy. On the contrary, when a metal ion is inserted at the center of the macrocycle, a redox reaction eliminates the hydrogen atoms as H₂, and all the N atoms become equivalent. Fig. 1 shows the N 1s core level photoemission spectra of 2H-TPP monolayers deposited at room temperature on Ni(111), Fe(110) and Ag(111) compared with the spectrum of a 2H-TPP multilayer. It is evident that, while in the multilayer and monolayer on Ag(111) the N 1s spectrum is composed of two peaks, corresponding to non equivalent iminic (397.9 eV and 397.6 eV, respectively) and pyrrolic (399.9 eV and 399.6 eV, respectively) nitrogen atoms, both in the case of Ni(111) and Fe(110) substrates the spectra consist of one single peak (at about 398.5 eV). This is the clear confirmation that Fe-TPP and Ni-TPP are formed. Energetics obtained by Density Functional Theory calculations confirms that this redox reaction happens on Fe and Ni substrates at room temperature. In particular, for the most critical case, Ni(111), the calculations demonstrate that the redox metalation reaction would be exothermic with an energy gain of 0.89 eV upon embedding Ni ad-atom in the macrocycle (see Fig. 2). In the monolayer regime upon adsorption at room temperature, TPP exhibits a conformational adaptation with a considerable rotation of the phenyl substituents with respect to the macrocycle plane, mainly due to the steric effect of hydrogen atoms. This causes the macrocycle to be at a distance d between 2.5 Å < d < 5 Å depending also on the possible distortion of the macrocycle ring. Our data indicate that, even considering the large macrocycle distance, the metalation may occur. Obviously, this does not happen on all substrates, as demonstrated by the Ag and even Au cases, although both Ag and Au form stable metallo-porphyrin complexes. This is a novel way to form, via chemical modification and supramolecular engineering, metal–organic networks on magnetic substrates with an intimate bond between the macrocycle molecular metal ion and the substrate atoms. The achievement of a complete metalation by Fe and Ni can be regarded as a test case for successful preparation of spintronic devices by means of molecular-based magnets and inorganic magnetic substrates.

Figure 2. Top view (top) and side view (bottom) of the equilibrium geometries for the 2H-TPP molecule adsorbed on Ni(111) in presence of a Ni ad-atom (a) and in case of incorporating the Ni ad-atom (b). The reaction is exothermic from (a) to (b) with a gain in energy of the system of 0.89 eV. Adapted with permission from DOI:10.1021/nn304134q. Copyright 2012 American Chemical Society.
Spin-Dependent Electron Correlations in Itinerant Ferromagnets

Spin selectivity in angle-resolved Auger Photoelectron Coincidence Spectroscopy (AR-APECS) has been used to probe electron correlation in ferromagnetic Fe/Cu(001) thin films. By disentangling contributions to the two-hole finale state which arise from different spin combinations of holes in the majority or minority bands, a strong correlation has been measured only when both holes originate in the majority band. Such a result indicates a different degree of electron localization in the majority and the minority bands.

In Core-Valence-Valence (CVV) Auger decays, two holes are created in the valence band (VB). In conventional Auger spectroscopy, only one of the two electrons leaving the VB is measured (i.e. the Auger electron) and consequently many details of the electron filling the core hole are lost. In AR-APECS (Angle Resolved - Auger PhotoElectron Coincidence Spectroscopy), the coincident detection of the Auger electron and its parent photoelectron allows one to put constraints on the electron which leaves the valence band and fills the core hole, thereby getting information on the total spin value of the two-hole finale state and providing new insights in the study of magnetic systems.

In addition, the CVV Auger line shape is sensitive to electron-electron correlation and can be well-understood within the well-established Cini-Sawatzky approach. If the two holes are independent, as in the case of non-correlated materials, the Auger line shape is well-described by simple Self-Convolutions of the valence Density Of States (SCDOS). On the other hand, when hole-hole repulsion is significant, the line shape is distorted, giving rise to sharper features located at lower kinetic (higher binding) energy in the Auger spectra of highly correlated materials. Ultimately, band-like versus atomic-like behaviors are respectively ascribed to the two limit cases.

The combination of spin selectivity and sensitivity to electron correlation become relevant in the study of itinerant ferromagnets, where the majority spin and minority spin split valence sub-bands have significantly different DOSs. In this case one has the possibility to pick two electrons out of the valence band, so that the two-holes in the Auger final state can have different spin pairings, depending on which sub-

![Figure 1. AR-APECS of Fe on a 3 ML thick Fe/Cu(001) film: green triangles and red circles are experimental data in the two angular configurations enhancing high spin and low spin contributions, respectively. The resulting spin contrast, allows one to assign the four contributions (possible combinations of “up” and “down” holes) to the Auger decay depending on where the two holes originated, that is, in terms of the majority band (blue lines), the minority band (pink dashed lines), or a mixed contributions (magenta dashed-dotted lines). Adapted from DOI:10.1103/PhysRevLett.109.126401.](image-url)
band each hole originated in, and thereby probe electron correlations in each sub-band. In the present work, AR-APECS measurements have been performed on a ferromagnetic, 3 Monolayers (ML) thick, Fe film grown on Cu(001). Fe 3p\textsubscript{3/2} photoelectrons, exited by 250 eV linearly polarized photons, have been detected in time coincidence with Fe M\textsubscript{23}V Auger electrons at two different angular configurations: one enhancing high spin final states and the other favoring low spin states. If we refer to as “up” the holes created in the majority band, and “down” the holes created in the minority band, we have then four possible spin combinations for the Auger two-hole final state: “up-up”, “up-down”, “down-up” and “down-down”. Due to an interplay among photoemission selection rules, Auger matrix elements and the angular distribution of the emitted electrons, one obtains that up-down and down-up contributions are relatively higher in the experimental configuration favoring low spin states, while up-up and down-down contributions become relatively more important in the geometry favoring high spin states. Fig. 1 shows AR-APECS spectra of the Fe M\textsubscript{23}V Auger spectrum obtained in the low-spin (red symbols) and high spin (green symbols) geometries. Fig. 2 shows the spin-resolved DOS obtained by ab-initio calculation within the spin polarized density functional theory. The dashed curves of Fig. 1 show the SCGOS for the four possible spin combinations of final state holes based on the DOS of Fig. 2. It is evident that the ~ 37 eV feature enhanced in the high-spin spectrum is not reproduced. However, by applying the Cini-Sawatzky approach only to the up-up contribution, as shown by the solid blue curve, the entire spectrum is now accounted for. Here the relative intensities are estimated by fitting the experimental data in order to emphasize how the energy position of the four features is affected by the spin-splitting and the electronic correlation; in the original paper they have been calculated ab-initio in order to provide also a first quantitative account for the spin selectivity mechanism in AR-APECS. The need to employ the Cini-Sawatzky model indicates significant correlation between two holes in the majority band: to obtain agreement with the experimental feature, we find that this correlation energy has a value \(U = 2.7\) eV.

Different degree of localization of differently spin oriented electrons, by an amount which depends on the size of the system, may have a relevant impact in magnetic nano-devices and spintronics.

Figure 2. Calculated spin-resolved DOS of the 3 ML thick Fe film used to deconvolve the AR-APECS experimental data. Adapted from DOI: 10.1103/PhysRevLett.109.126401.

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Original Paper

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We report a multiscale investigation of N,N’-bis(n-octyl)-x:y, dicyanoperylene-3,4:9,10-bis(dicarboximide), PDI8CN2, n-type semiconductor, consisting in the characterization of the crystallographic structure and morphology of molecular films. GIXRD (Grazing Incidence X Ray Diffraction) and AFM (Atomic Force Microscopy) measurements reveal that the crystalline order and the growth mechanism of PDI8CN2 films depend on the deposition temperature. We show how these features are highly correlated with the electrical response of PDI8-CN2-based field-effect transistors.

In recent years, organic semiconductors (OSCs) have been the subject of growing scientific and technological interest. Compared with traditional silicon electronics, devices based on OSCs have appealing characteristics, such as light weight, mechanical flexibility and low-cost production. These advantages make them promising candidates for a wide range of applications from displays to sensors. In these systems, the charge mobility depends on the overlap between π-orbitals of vicinal molecules, which is intrinsically correlated with the microscopic structure and density of structural defects of the organic films. The structure of the first molecular layers may be significantly different from the bulk structure because of the interaction between the organic molecules and the substrate. Therefore, the determination of the molecular orientation and packing of organic molecules in thin films is a fundamental information for modelling accurately their electronic band structure and the associated intrinsic charge-transport properties.

Among n-type OSCs, the PDI8CN2 molecule has been reported to allow the fabrication of OFETs (Organic Field-Effect Transistors) with excellent electrical performance and remarkably high stability in air. In spite of the potential applications of PDI8CN2, the knowledge of the crystal structure, molecular conformation and their relationship with the multiscale organization in the film phase were still missing. In this work we fill this gap by using a multiple technique approach which allowed the OFET response to be understood.

The molecular packing of the bulk material was investigated by coupling x ray powder diffraction technique with ab initio and molecular-mechanics calculations. We assessed the triclinic structure schematically drawn as depicted in Fig. 1a and b. GIXRD measurements, collected at XRD1 Elettra beamline, were fundamental for determining the PDI8CN2 film structure. Fig. 1c shown an example of 2D-GIXD image for a 100 nm-thick film sublimed on SiO2/Si substrate at

**Figure 1.** a) Schematic drawing of the crystal structure of PDI8CN2, viewed down [100]; horizontal axis = b. b) π–π stacking of the flat perylene cores in the ABCA sequence (side chains omitted for clarity). c) 2D-GIXD experimental images of 100nm-thick PDI8CN2 film grown at 120°C. d) Simulated 2D-GIXD image reproduced by using the bulk structure and [001] texturing. Adapted from DOI: 10.1002/adfm.201101640, Copyright 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
substrate temperature ($T_{\text{sub}}$) = 120 °C. From the position of the Bragg spots the unit cell parameters were extracted. Their values surprisingly match those of the bulk phase, differently from what observed for other perylene derivative molecules which arrange in a characteristic structure (referred to as thin film phase) when deposited on a substrate. From the 2D-GIXRD image analysis we found that PDI8CN2 film is 2D-polycrystalline and molecules arrange with a π-π stacking geometry lying within the film plane, as confirmed by the good agreement between the simulated (Fig. 1d) and the experimental images. This is the successful configuration for having good OFETs charge mobility.

We found that the crystal structure of PDI8CN2 films does not change as a function of the film thickness, $t$, and of the substrate temperature during the deposition, $T_{\text{sub}}$, proving evidence for the lack of a thin film phase. Indeed, 2D-GIXRD images collected for films prepared under various experimental conditions show the invariance of the Bragg spots position (Fig. 2). The intensity and shape of Bragg revealed that films grown at higher $T_{\text{sub}}$ comprise bigger crystal grains with high crystalline order and orientation.

The morphology of the PDI8CN2 films, characterized by AFM, revealed a clear dependence on both $T_{\text{sub}}$ and $t$. Regardless $t$, by increasing $T_{\text{sub}}$, bigger grains are formed, meaning that the film shows a better quality and a lower density of defects, resulting from the reduced number of grain boundaries. From the analysis of the surface roughness versus $t$, the growth mode was estimated: at high $T_{\text{sub}}$ a layer-by-layer mechanism dominates, whereas a 3D-growth mode occurs at 25°C.

The different growth mechanisms result in the morphological and structural features of the resulting films and appear to be correlated with the trend of the electrical parameters measured in PDI8CN2-based OTFTs. Indeed, higher crystallinity, lower misorientation (i.e. molecular π-π stacking maintains its orientation parallel to the substrate surface) and lower grain boundaries density were proved to be the cause of the higher mobility recorded for the PDI8CN2 FETs.

![Figure 2](image-url) a–f) 2D-GIXD images of PDI8CN2 films with nominal thickness of 10, 40 and 100 nm, sublimated on SiO2/Si at 25°C (a–c) and 120 °C (d–f). Adapted from DOI: 10.1002/adfm.201101640, Copyright 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Original Paper

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We provide evidence for the formation of a bilayer graphene on the Ru(0001) surface, which arises only after large ethylene exposures. Angle-resolved photoemission spectroscopy highlights the formation of a single Dirac state with nearly freestanding character and $p$-type doping. Complementing scanning tunneling microscopy measurements show that this new phase consists of weakly interacting graphene layers arranged in an AA stacking sequence. These features sizably differ from those of bilayer graphene synthesized on Ru(0001) at much smaller ethylene exposures.

The electronic properties of graphene - a single layer of carbon atoms arranged in a honeycomb lattice - strongly depend on the interaction with the supporting substrate. When graphene is placed on top of another graphene layer in a Bernal (AB) stacking, the weak interlayer coupling is sufficient to modify the dispersion of the charge carriers from linear (massless fermions) to hyperbolic (massive chiral fermions). A suitable way to reduce this interaction and restore a nearly freestanding band behavior in graphene is to introduce a relative displacement of the two layers. We were able to synthesize a bilayer graphene phase with these structural and electronic properties on the Ru(0001) surface by performing a large ethylene exposure. This novel phase displays an AA stacking sequence and a relatively weak structural modulation, that result in a $p$-doped and linearly dispersing Dirac state.

At an exposure level of $10^2$ L of ethylene the Ru(0001) surface held at a temperature of 1600 K allows the formation of a full graphene layer in contact with the metallic substrate, plus patches of a second graphene layer. In an angle-resolved photoemission spectroscopy map along the $\Gamma K$ direction of the graphene Brillouin zone (Fig. 1a) the respective band features are identified as the parabolic-like $\pi_1$ and $\pi_1^*$ states, ascribed to the first graphene layer, and the sharp and $n$-doped $\pi_{2c}$ Dirac cone and $\sigma$ band, accompanied by several replicas, which are associated to the patches of the graphene bilayer. Figs. 1b and 1c display the changes occurring in the electronic structure of the system upon further exposure to $10^5$ L of ethylene with the Ru surface at 1600 K. In addition to the previously observed bands, we find a new $\pi$ state ($\pi_{2F}$), whose properties are better captured in the energy distribution curves presented in Fig. 1d. The $\pi_{2F}$ state displays a linear dispersion, characteristic of a free-standing graphene layer, with a Dirac point above the Fermi level ($p$-type doping). An energy gap $\Delta$ between the $\pi_{2c}$ and $\pi_{2c}^*$ of 200 ± 30 meV at the K point (blue curve) is also observed.

Figure 1. (a) Second derivative of the angle-resolved photoemission spectroscopy intensity map along the $\Gamma K$ direction of graphene for the low-exposure sample. (b) Raw and (c) second derivative angle-resolved photoemission spectroscopy intensity map for the high-exposure sample. (d) Energy distribution curves from the spectra enclosed by the red rectangle in panel (b). Reprinted with permission from DOI: 10.1021/nn303821w. Copyright 2012 American Chemical Society.
Fig. 2a shows a scanning tunneling microscopy image for the sample exposed to $10^5$ L of ethylene. The first graphene layer displays the (23×23) moiré pattern resulting from the lattice mismatch between Ru and graphene. Additional structures, exhibiting different surface reconstructions, are identified as second layers of graphene.

The 2C phase (lower left part of the image) displays a moiré pattern with a maximum corrugation of 1.1 Å and an apparent height 3.3 Å (Fig. 2b), closely corresponding to the distance between the atomic layers in graphite. Instead, the novel 2F phase (right-hand side of Fig. 2a) displays a much weaker moiré contrast (0.05 Å) and a smaller apparent height (2.1 Å).

High-resolution scanning tunneling microscopy measurements (Figs. 2c and 2d) point out the origin of these differences. In the 2C phase the graphene layers are AB-stacked, with the two carbon atoms of the unit cell lying at a distance of 25 pm (Fig. 2e). We notice that the degeneracy between the two carbon sub-lattices of the 2C phase is responsible for the band gap $\Delta$ between the $\pi_{2C}$ and $\pi_{2C}^*$ states observed in Fig. 1. In the 2F layer, instead, the carbon atoms lay on the same plane (in Fig. 2f the relative distance is reduced to 4 ± 7 pm), thus supporting an AA stacking of the graphene layers in this novel bilayer phase. Our results prove that the first graphene layer grown on Ru(0001) can be used as a template to grow different phases of graphene bilayers.

**Figure 2.** (a) Constant-current scanning tunneling microscopy image of graphene on Ru(0001) showing different phases of graphene multilayers. (b) Apparent height profile along the red line displayed in (a). (c) and (d) High-resolution scanning tunneling microscopy image for 2C and 2F, respectively. (e) and (f) Apparent height profile along the blue and green lines displayed in (c) and (d), respectively. Adapted with permission from DOI: 10.1021/nn303821w. Copyright 2012 American Chemical Society.

**Original Paper**

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One of the most active areas of research in the field of materials chemistry applied to the production of energy concerns the development of more effective and cheap catalysts to be used in fuel cells, devices similar to batteries that convert chemical energy into electricity by exploiting the reaction of oxygen with a fuel, the most common of which is hydrogen. Both the oxidation of hydrogen at the anode and the reduction of oxygen at the cathode need suitable catalysts to promote the two half-reactions. The best oxygen reduction catalysts currently in use are based on platinum, but its high cost and durability issues stimulate the search for alternative, cheaper and possibly equally efficient materials.

A much-studied class of catalysts is inspired to the strategy that nature adopts to reduce atmospheric oxygen to water (e.g. in breathing). In the membrane of bacteria and in mitochondria within the cells of higher organisms this task is entrusted to extraordinarily complex enzymes, whose catalytically active “heart” consists of some heme molecules - coordination complexes formed by a cyclic organic molecule (a so-called “macrocycle”) named Porphyrin, at whose center sits an iron atom. This iron site in such a very special environment promotes the reduction of the oxygen molecule to two water molecules, producing the energy that is used for cellular metabolism. Chemists and materials scientists are therefore studying simplified synthetic analogues of heme as an alternative to platinum catalysts to promote the Oxygen Reduction Reaction (ORR): artificial Porphyrins (Pps) or the closely related Phthalocyanines (Pcs).

It was recently recognized that a major obstacle to a full understanding of the catalytic mechanisms and to the design of new and more efficient catalysts is the lack of detailed information about the active site structure and how this evolves when oxygen coordination occurs. Recently, we have provided precisely this information for a model system constituted by FePc deposited on a Ag(110) single-crystal substrate. By converging and coherent evidence from a rich set of complementary experimental results and calculations comprising STM (Scanning Tunneling Microscopy), XPS (X ray Photoelectron Spectroscopy), XAS (X ray Absorption Spectroscopy) and DFT (Density Functional Theory), the local chemisorption geometry of the catalyst molecule on the substrate in the catalytically active phase was elucidated and its evolution upon oxygen adsorption was revealed. The catalytically active FePc phase corresponds to slightly less than 1 Monolayer (ML) of FePc displaying a c(10×4) superstructure, with each FePc molecule sitting with its Fe atom on-top a substrate Ag atom.

When the sub-ML phase is exposed to oxygen, STM gives a characteristic and direct fingerprint.
of oxygen binding to FePc in the form of a bright/dim switch of the Fe-centred density of states (compare Fig. 1a and 1b). The switch is reversible: the bright bump reappears even at room temperature and during dosing. This shows that dim adsorbates are not thermodynamically stable. A labile Fe-O bond compatible with the reversible bright/dim switch was searched for by means of DFT calculations, which led to the so-called FePc-(η²-O₂)-Ag(110) coordination after oxygen dosage (Fig. 1b), where the Fe atom on-top an Ag surface atom is laterally coordinated by two oxygen atoms sitting at nearby Ag bridge sites. These pull the Fe atom downward, with a concomitant saddle-shaped distortion of the initially planar molecule.

To confirm this picture, high resolution XPS and XAS measurements were performed at the ALOISA beamline. Angle-dependent C 1s XAS data reported in Fig. 1c are fully compatible with the reversible out-of-plane distortion of the macrocycle upon oxygen dosing and subsequent annealing proposed on the basis of STM and DFT results. In addition, the reversible variation of the Fe 2p peak intensity in XPS spectra (not shown), explained as a photoelectron diffraction effect due to the changed Fe coordination, further confirms and sharpens the picture.

O 1s XPS spectra (not shown) show that oxygen reduced by the molecular catalyst in our ultra-high vacuum environment is left in the silver topmost layers, while in solution the oxide produced at the cathode surface is removed by protons provided from the anode. In order to remove this oxygen and fully close the catalytic cycle, low energy ion bombardment by means of ionized hydrogen has been used. The ion treatment almost exactly restores FePc molecules in their state prior to oxygen dosing (Fig. 1a, b), with no overall loss of catalyst. Cycles of oxygen dosing and removal can be repeated several times.

Figure 1. STM images of the catalytically active c(10x4) FePc/Ag(110) phase (a) prior to and (b) after oxygen dosing (30 × 30 nm²). Molecular models, high-resolution STM single molecule images and the corresponding simulated images based on DFT calculations are reported in the middle stripes. Bottom: side views of the molecular coordination to the substrate along the two main surface crystallographic directions (a) prior to and (b) after oxygen dosing. (c) Angle-resolved FePc C K-edge XAS spectra evolution upon oxygen dosing and subsequent annealing. Adapted from DOI:10.1038/NMAT3453

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X ray-based method to follow clusters of exogenous cells in small living animals

The actual knowledge of cellular processes in living beings with cellular resolution is limited and any improvement is a demanding challenge. The possibility to follow cells in living organisms over a long period of time would represent an opened window on complicated phenomena such as cell migration, cell homing, dynamics of tumor growth, metastatic spread and fate of injected stem cells. In this work we explored the possibility of using x ray computed tomography combined with gold nanoparticles contrast agent to retrieve the position of clusters of tumor cells in living mice with the aim to improve our knowledge of tumor behavior at high resolution.

The advent of nanotechnology in modern research has recently boosted the horizon of possibilities in the hands of researchers. In particular, nanotechnologies offer a number of new opportunities in applied biology. Nanomaterials like nanoparticles, quantum dots, nanorods etc. have a typical size between 1 and 100 nm, that is, several order of magnitudes smaller than a cell (about 10 µm). This permits one to use nanomaterials in interaction with single cells in new and versatile modes. Nanomaterials can be engineered ad hoc for various functions such as drug carriers, therapeutic and diagnostic tools, imaging agents etc. An example is the use of nanomaterials to label predetermined cells in living animals to follow their fate using an imaging technique (the so-called cell tracking). This permits one to understand in depth processes such as tumor growth, tumor metastasis, or to follow up stem cell-based therapy simply by following the marked cells positions over time.

X ray micro computed tomography (µCT) is a well-established imaging technique that permits one to reconstruct in 3D the position of cells using different x ray attenuation properties. In our experiments we exploit this property using gold nanoparticles (AuNPs) as cell contrast agent. AuNPs are an efficient attenuator for x rays at the diagnostic energy range, they have a good biocompatibility, and they are easy and cheap to produce. Therefore we chose AuNPs in order to increase the visibility of the cells in µCT.

Our procedure involves four distinct phases as depicted in Fig. 1. First, the cells are loaded with AuNPs (~50 nm in diameter) in vitro. The AuNPs internalization is facilitated by binding horse serum proteins to the AuNPs surface. The cells endocytose and phagocytose the AuNPs that are then stored permanently in the lysosomes. The marked cells (containing tens of thousands of AuNPs each) are then injected into the host.

![Diagram](image)

**Figure 1.** Scheme of the technique. Reprinted with permission from DOI:10.1016/j.nano.2012.06.004.
animal. The implanted cells then proliferate and, if tumor cells, may metastasize. The cellular contrast agent density is then diluted during the cellular proliferation. Clearly, the dilution decreases the visibility of the cell on the CT images but give us an indication to the number of mitoses undergone by the cells. Finally, one or more µCT scans can be acquired in intervals after cell implantation or transplantation to visualize where the injected cells have gone. In the presented experiment (run as proof of principle of the technique) we used F98 tumor cells injected into mice. The in vivo µCT was acquired between 6.5 and 8.5 days after the injection of cells. Particular attention was paid to the x ray dose delivered to the animals. High x ray dosage is harmful to the animals. It induces cell damage and can compromise the experimental results. This is of particular concern since the higher the resolution attained the higher the x ray dose required. Therefore the µCT was restricted to 100 mGy that is considered a low x ray dose for repeated µCT on the same animal. The x ray dose restriction limited the best resolution possible to about 100 µm that translated into a detection of cell clusters of about 10 cells in diameter. The difference is shown in Fig.2 where the 3D rendering of the mouse head acquired in vivo (at low x ray dose; Fig2a and Fig2c) and ex vivo (at high x ray dose; Fig2b and Fig2d) are compared. The study demonstrated for the first time the feasibility of x ray µCT cells detection in vivo and set the limitations due to the x ray dose restrictions for longitudinal studies that are necessary for cell tracking experiments. A similar study can be conducted using marked stem cells to evaluate their distribution during a treatment with the advantage of a significant less dilution of the AuNPs due to the slower proliferation rate of stem cells.

![Figure 2. Comparison of two 3D renderings of a CT of a mouse injected with AuNPs loaded cells depicts (A–C) the low x ray dose in vivo and (B–D) the high x ray dose ex vivo data. Reprinted with permission from DOI:10.1016/j.nano.2012.06.004.](image-url)
Identification of cell cycle stage using IRMS on B16 melanoma live cells

In this work, we show a novel way of determining the cell cycle stage on B16 mouse melanoma live cells using Fourier Transform Infrared Microspectroscopy (IRMS) on asynchronous, S- and G0- synchronized cells’ population. Our IRMS results were cross-checked in parallel with Flow Cytometry (FC), a widely used technique in biology to assess cell cycle. In order to perform these experiments, a new generation of microfluidic devices (MD) on silicon coated - BaF2 optical windows were fabricated and used.

The label-free, non-invasive and non-damaging capabilities of infrared microspectroscopy (IRMS) have been recently employed to study cellular biology at diffraction-limited spatial resolution achieving sub-cellular details thanks to the high brilliance of IR synchrotron radiation (SR) sources. However, all measurements have been limited to fixed cell samples due to the so-called water absorption barrier. Live samples need to be in an aqueous environment without exception and unfortunately, in Mid-IR, water absorbs in the same regions of biological interest. The possibility of monitoring live cells under physiological conditions to track their induced or naturally occurring biochemical modifications is definitely a turning point for the full exploitation of IRMS diagnostic capabilities. Our lab, in collaboration with the micro-nanofabrication team at IOM-CNR has developed CaF2 and BaF2 microfluidic devices (MD) suitable for IRMS of live cells. The microfabrication approach we have proposed offers unique design flexibility and environmental control, which greatly improves accuracy on the water subtraction.

In this work, we exploited this technique for the assessment of cell cycle stage of live B16 mouse melanoma cells. Cellular proliferation, transformation and death are regulated events at the basis of organism life and the interplay between them is of paramount importance for hindering diseases occurrence and progression and eventually being able to guarantee a successful therapy. The knowledge of cell cycle phase distribution is preeminent for understanding cellular behaviour under normal and stressed conditions. These tasks are commonly achieved using Flow Cytometry (FC) or immunohistochemistry which usually requires fixation. In this work, results and information for assessing the cell cycle stage distribution obtained by FC and IRMS analysis of live cells were compared.

In particular, asynchronous, S- and G0-synchronized B16 mouse melanoma cells were studied by running parallel experiments based on IRMS in microfluidic devices (MD-IRMS) and FC using Propidium Iodide (PI) staining cellular DNA. Hierarchical Cluster Analysis (HCA) of cellular microspectra in the 1300–1000 cm⁻¹ region pointed out a distribution of cells among clusters, which was in good agreement with FC results among G0/G1, S and G2/M phases (see Fig. 1a-f). The differentiation was mostly driven by the intensity of Ph1 (phosphate I) and PhII (phosphate II) bands, assigned to the asymmetric and symmetric stretching of phosphate moieties of nucleic acid backbone. In particular, Ph1 almost doubled from the G0/G1 to G2/M phase (see Fig. 1g-i), in agreement with the trend followed by nucleic acids during cellular progression showing for the first time that IRMS accuracy is comparable to that of FC when assessing cell progression.

The analysis of the cluster centroids of synchronized G0 (SynG0), synchronized S (SynS) and asynchronous (Asyn) populations pointed out comparable intensity variations of the lipid bands related to aliphatic chains, showing a progressive increase of the 2990-2800 cm⁻¹ spectral area from G0/G1 to G2/M phase. The previous trend was detectable also for phospholipids, as deduced from the intensity variations of the carbonyl ester band, centred at 1743 cm⁻¹ for all cell cycle phases. Similar consideration could be
drawn out for the broad regions ranging from 1590-960 cm\(^{-1}\) and 1720-960 cm\(^{-1}\). The overall increase of spectral absorbance was in agreement with the mass increase of the cell before mitosis, as has been reported by other authors.

It is noteworthy that B16 cells have been measured immediately upon trypsinization, without letting them adhere onto the substrate. In these conditions, B16 are spheroids, the average diameter of which is slightly bigger that the optical path constrained by the fluidic cell. Therefore, we believe the contribution to intensity increase from possible cellular thickness variations during cell cycle progression is minimal.

Overall, both FC and IRMS are multiparametric techniques that give a broad range of information at the same time. Actually, IRMS is less selective and slower than FC, but it is a label-free technique that lately has become applicable on live cells thanks to the optimization of devices and methodologies. Indeed, biochemical artefacts, induced by permeabilization protocols used for promoting dye penetration, are totally avoided in MD-IRMS. The possibility to exploit the advantages offered by synchrotron radiation fosters the upgrade of IRMS to a label-free single cell based assay, opening new and fascinating scenarios for the real-time analysis of live cells under physiological conditions.

**Figure 1.** (a-c) Distribution of cells’ population in different phases of the cell cycle. Cells synchronized in G0 (SynG0), in S phase (SynS) and asynchronous cells (Asyn) were collected and analyzed by FC upon PI staining. Representative histograms showing the number of cells with different red-fluorescence intensity, proportional to the DNA content are shown. Results of independent synchronization experiments are summarized as percentage of cells in each phase. (d-f) Dendrograms showing the results of HCA analysis on absorbance spectra for SynG0, SynS and Asyn experiments respectively. (g-i) Cluster centroids for SynG0, SynS and Asyn preparations are shown in the 1275-1000 cm\(^{-1}\) region. Each cluster is plotted with shadow representing the standard deviation. Reproduced from D.E. Bedolla et al., Analyst 138, 4015 (2013), with permission of the Royal Society of Chemistry.

**Original Paper**

D.E. Bedolla et al., Analyst 138, 4015 (2013); DOI: 10.1039/c3an00318c
A 6500-year-old human mandible from Slovenia has been studied using different analytical methods. The results have shown that the left canine, in particular an area of dentine resulting from occlusal wear and the upper part of a vertical crack, was filled with beeswax. The intervention was likely aimed to relieve tooth sensitivity derived from either exposed dentine and/or the pain resulting from chewing on a cracked tooth: this would provide the earliest known direct evidence of therapeutic-palliative dental filling.

Previous archaeological finds suggest that Neolithic people could have practiced therapeutic dentistry. In 2006 Coppa and his group found several holes (probably made using a bow drill) in human molars from a 7500 to 9000-year-old graveyard in Pakistan, but there was no evidence of dental filling (Coppa et al., *Early Neolithic tradition of dentistry*, Nature 440, 775 (2006)).

The present study, involving several research groups and using an integrated multi-disciplinary approach, provides direct evidence of the earliest therapeutic dental filling ever discovered. The discovery is based on the finding of an extraneous material on the occlusal surface of a canine from a Neolithic human mandible. The jawbone fragment, bearing a canine, two premolars, and the first two molars, was found in 1911 near the village of Lonche in northern Istria (Slovenia) and kept since in the Natural History Museum of Trieste (Italy). The data for the study were obtained using conventional and synchrotron radiation computed x ray microtomography (micro-CT), radiocarbon dating with accelerator mass spectrometry (AMS), infrared (IR) spectroscopy and scanning electron microscopy (SEM). These advanced analytical techniques provided crucial information on morphology and age of the mandible, age and composition of the dental filling and tooth microstructure. Conventional x ray micro-CT (performed at the Tomolab station of Elettra) provided a high-resolution 3D reconstruction of the mandible (Fig. 1). In particular, we could observe that the canine revealed a long vertical crack, and that an area of enamel had worn away exposing the dentine (Fig. 2a). To increase the spatial resolution and obtain more detailed images, the tooth crown was then investigated using synchrotron x ray micro-CT at the SYRMEP beamline of Elettra (Figs. 2b, 2c). Thanks to the high spatial coherence properties of synchrotron radiation, we could use phase-contrast imaging to visualize an unusual light material forming a thin cap that perfectly filled the cavity and the upper part of the canine crack.

A minute amount (volume < 2 mm³) of the filling material was extracted from the canine, placed in a diamond anvil cell, and layered to allow an analysis in transmission in the mid-infrared spectral range (4000-500 cm⁻¹) (Fig. 2e). A set of standards, including modern natural beeswax, was run in a

![Figure 1.](image)

**A combination of modern physics tools reveals the oldest dental filling**
second step to fingerprint the unknown substance. Thanks to the high molecular sensitivity of the IR technique, the analysis revealed that the chemical markers (spectral features of wax ester compounds) of the tooth filling corresponded to beeswax, with some additional bands revealing the presence of salts and oxidation processes, as expected after such ageing period. Radiocarbon dating was performed with AMS in two independent laboratories. A bone sample of about 1 g was collected from the mandible using a conventional hand drill, its collagen was then extracted and subsequently measured by means of the CIRCE AMS system at the 2nd University of Naples (Caserta, Italy). A beeswax sample of 1.4 mg was finally extracted from the tooth and AMS 14C measurements were performed using the STAR facility at ANSTO. The AMS measurements determined that both mandible and beeswax filling were about 6,500 years old. SEM images showed in detail the morphology of the tooth occlusal surface, demonstrating that beeswax not only filled the exposed area of the dentine, but also penetrated the longitudinal crack. The observation of the edges of the crack, before and after beeswax cleaning, has given information to assess whether the fracture originated antemortem, perimortem or postmortem. The evidence obtained in this study, based on the use of advanced analytical methods, was finally interpreted with the involvement of medical dentists and palaeoanthropologists. In conclusion, the data strongly support the hypothesis of therapeutic dental treatment, likely used to alleviate the pain of chewing on a cracked tooth, although alternative postmortem practices cannot be completely ruled out. However beeswax may have been used to plug the cracked and worn tooth while its owner was still alive, which would make it the earliest known direct evidence of a therapeutic dental filling.

Figure 2. a) Conventional micro-CT virtual section of the Lonche canine (voxel size: 18 μm). b) Synchrotron x ray micro-CT longitudinal section showing details of the crown: the thickness of the filling material (colored in yellow), afterward identified as beeswax, is visible. Beeswax exactly fills the shallow cavity in the exposed dentine and the upper part of the crack (voxel size: 9 μm). c) Synchrotron x ray micro-CT transversal slice of the tooth showing the enamel crack. d) Microphotograph of the tooth crown with indication of the surface covered by beeswax (within the yellow dotted line). e) Comparison between the IR spectrum of the material filling the Lonche canine (average of 10 spectra, 128 scans per spectrum, 4 cm⁻¹ spectral resolution) and a modern sample of natural beeswax. Adapted from F. Bernardini et al., PLoS ONE 7, e44904 (2012); DOI: 10.1371/journal.pone.0044904

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Topoisomerase I inhibitors are an important class of anti-cancer drugs that work by disrupting DNA replication. We found that the cancer cells’ replication machinery can react to DNA topoisomerase I inhibitor-induced DNA damage with a repair process called “fork reversal”. In this work, we provide the first description of the mechanism of “fork reversal” and of the factors that control it. These studies offer new molecular perspectives to create more effective and specific therapies based on agents that inhibit DNA replication.

In particular, RECQ1, which is an enzyme that plays a key role in the maintenance of genome stability, appears to be responsible for restarting the reversed replication forks once the TOP1 induced lesion has been repaired. Thus, the reversed forks cannot restart without the help of RECQ1. On the other hand, PARP activity stabilizes forks in their regressed states by limiting their restart by human RECQ1, thus preventing the restart of reversed forks by RECQ1 before the lesion is repaired.

Most cancer chemotherapeutics act by inhibiting DNA replication. The drugs aim to target highly proliferating cancer cells rather than normal cells, but unfortunately many also are toxic for normal cells. Cells, both healthy and cancerous, reproduce by replicating their DNA. Anti-cancer drugs like topoisomerase I (TOP1) inhibitors work by disrupting DNA replication in cancer cells. Topoisomerases release torsional stress during DNA replication by temporarily cutting the rope of DNA, letting it untwist, and putting it back together again. Scientists’ understanding of how TOP1 inhibitors work has, however, been incomplete. The working theory has been that TOP1 inhibitors leave a nick on one of the DNA strands by inhibiting the ability of the topoisomerase to seal the broken DNA. When the replication machinery collides with this nick, a double strand break occurs which stops the replication process. Double strand breaks are the worst kind of DNA lesions because both strands are compromised and require an intricate DNA repair pathway to be fixed.

Our findings suggest that cancer cells are much “smarter” than originally thought and have a strategy to deal with this scenario. When TOP1 inhibition causes “replication stress” in the form of a nick on the DNA, the replication machinery pauses and reverses its course instead of colliding with the TOP1 induced DNA lesion (Fig. 1). This mechanism of “replication fork reversal” gives time for the lesion to be repaired, so that replication can continue on again, preventing the hoped-for double strand break. In fact, not only does the strand halt when it reaches the nick, but it senses the problem ahead of time, coming down the line. The replication structure does not operate blindly, but has advance notice of the injury, which gives it time to halt and repair the lesion before it reverses course and move into forward gear again.

This is important because it is the first evidence showing that cancer cells’ DNA replication machinery can react to drug treatment through fork reversal. Our group also uncovered the mechanism to restart the replication forks that have reversed upon TOP1 treatment (Fig. 2). We found that two important cellular proteins, PARP and RECQ1, control the fork reversal and restart mechanism.

In particular, RECQ1, which is an enzyme that plays a key role in the maintenance of genome stability, appears to be responsible for restarting the reversed replication forks once the TOP1 induced lesion has been repaired. Thus, the reversed forks cannot restart without the help of RECQ1. On the other hand, PARP activity stabilizes forks in their regressed states by limiting their restart by human RECQ1, thus preventing the restart of reversed forks by RECQ1 before the lesion is repaired.

**Figure 1.** Representative electron micrograph showing the image of a reversed replication fork. D, daughter strand; P, parental strand; R, reversed arm.
Having identified a specific and controlled biochemical activity that mediates this process offers new molecular perspectives to potentiate chemotherapeutic regimens based on TOP1 inhibitor treatment. For example, we can return to the approach of encouraging a “fatal” double strand break for cancer cells by combining TOP1 inhibitors with novel inhibitors of the proteins that control the process of replication fork reversal and restart. In addition, inducing replication fork reversal by TOP1 inhibitor treatment and impeding reversed replication fork restart by RECQ1 inhibition should also stop DNA replication, thus allowing clinicians to use lower TOP1 inhibitor doses, which, in turn, would mean fewer side effects.

Building upon this discovery, our next step is to determine if this mechanism holds true not just in response to TOP1 inhibitors, but also with other cancer drugs, a finding that would broaden the significance of our work even further. Another important step will be to search for other factors that control the replication fork reversal process, findings which would offer additional opportunities to disrupt the process.

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Crystal structures of human legumain unveil activation mechanisms to distinct peptidase activities

The cysteine protease legumain is a key player in immunity and cancer at different cellular locations, some of which are incompatible with its pH-stability. We solved the crystal structures of zymogenic and active legumain, unveiling its activation and regulation principles. Legumain contains an Asn-specific endopeptidase activity that is electrostatically released at acidic pH. Surprisingly, we uncovered a complementary proteolytic activation route, generating a carboxypeptidase activity. The context-dependent activation of legumain reconciles its partly conflicting moonlighting activities.

Biological signaling involves a complex network of decision making and signal transduction that must be regulated by proteases, key players in health and disease. The lysosomal cysteine protease legumain, synonymously termed the asparaginyl-specific endopeptidase (AEP), exemplifies how complex multi-branched processes combine in zymogen activation and activity regulation. These principles are essential to fulfill its demonstrated roles in (auto-)immunity and cancer involving manifold processes such as antigen processing; TLR processing and activation; or modulating tumor- and stroma-derived components of the cancer degradome. However, the exact mechanism of the activation process and the resulting consequences on legumain activity and localization remained unclear. Therefore we set out to study biochemical and structural properties of human (pro)legumain to get an in-depth understanding of its enigmatic autocatalytic activation and activity regulation principles. We successfully established a recombinant protein production strategy based on expression in *Leishmania tarentolae*. Subsequently, biochemical studies uncovered (1) an additional autocatalytic cleavage site at the C-terminus, (2) trans and cis processing during autoactivation, (3) insufficiency of proteolytic processing for activation, (4) a pH- and substrate-dependent $k_{cat}$ specificity and (5) ligand-mediated stabilization of active legumain at neutral pH. We were successful in crystallizing pH activated legumain (AEP) in complex with covalent active site-directed inhibitors. Anomalous phasing after mercury soaks led to an initial model of the enzyme. The crystal structure of active legumain revealed a caspase like overall structure with a zwitterionic S1 specificity pocket explaining legumain’s preference for Asn over Asp at P1 position at

**Figure 1.** Structure and regulation of (pro-)legumain. (A) Prolegumain consists of a caspase-like asparagine-specific endopeptidase (AEP) domain, an AP (activation peptide) and an LSAM (Legumain Stabilization and Activity Modulation) domain. The catalytic Cys189 is indicated in sticks representation. (B) $k_{cat}$ substrate specificity is implemented by Glu190. Top-view on the AEP active site shows how Glu190 stabilizes the protonated state of Cys189 Sγ. Neutralization or charge reversal at position 190 can be accomplished by substrates presenting positively charges residues at P1' – P2' positions. A substrate spanning the P4 – P3' positions (YVAN|AEA) was modeled based on the crystal structure of legumain in complex with the covalent YVAD-cmk inhibitor. Charged residues in close proximity to Cys189 (i.e at the primed sites) will regulate the substrate turnover speed ($k_{cat}$) by modulating the local pKa of Cys189 Sy.
pH 5.5. We identified Asn42 as third member of a catalytic triad and His148 as part of a trivalent oxyanion pocket. Moreover, we could uncover a $k_{\text{cat}}$-specificity filter that is implemented via Glu190 (Fig. 1).

On top of that, we succeeded in crystallizing the enzymatically inactive prolegumain. Prolegumain comprises of the AEP domain and a C-terminal prodomain positioned on top of the active site (Fig. 1A). The prodomain can be further segmented into a latency conferring activation peptide (AP) and an LSAM (Legumain Stabilization and Activity Modulation) domain. Surprisingly, we identified a death domain (DD) like fold of the LSAM domain albeit with different connectivity of the DD-helices that is additionally stabilized by two disulfides. The LSAM domain serves as an electrostatic stabilizer of the AEP domain at neutral pH by triggering an electrostatically encoded stability switch (ESS) localized near the AEP active site. Furthermore, substrate access in prolegumain is prohibited by the AP on the non-primed side and the LSAM domain on the primed side. Completely unexpectedly, we could show that prolegumain can be proteolytically activated to an asparaginyl-specific carboxypeptidase (ACP) at (near) neutral pH which remains electrostatically stabilized by the LSAM domain (Fig. 2). Besides its role in AEP-stabilization, we identified a double arginine motif on the LSAM domain, characteristic for carboxypeptidases. The distinct activation intermediates of legumain differ in both their biophysical and enzymatic properties and thus help to reconcile its partly conflicting moonlighting activities and localizations. Context dependent proteolytic and electrostatic activation routes explain for the first time seemingly contradictory functions of legumain in the extracellular space or the nucleus, as observed in solid tumors. Moreover, the analogy in domain architecture between legumain and caspases may bear reciprocal consequences with respect to component recruitment and activity modulation.

In summary, the here presented work provides for the first time a rational for legumain functions at different cellular locations incompatible with AEP's pH-stability. Direct stabilization of the AEP domain by ligands like the LSAM domain or allosterically by integrin binding enables the enzyme to be an active protease also at neutral pH environments.

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**Original Paper**

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Hydrogen bonds (HB’s) dynamics is currently recognized as the driving mechanism of many physical and biological processes. For instance, the thermodynamic behavior of HB in biological molecules has been the subject of intense studies in order to shed light on their role into the functionality issue. However, it is still not possible to separately quantify the different HB contributions to the free energy that defines the biochemistry of a given biomolecule. The main reasons basically relies on the complexity of the molecular structure. The capability to determine the single HB “strength” as a function of temperature is one the challenges that biophysicists are facing off. Measurements of free energy variations have been mainly carried out through differential scanning calorimetry (DSC) experiments, which measure the total free energy and cannot be employed to determine the distinct contributions of single bonds. An estimation of the HB energy can be provided from the temperature dependence of the bond’s lifetime ($\tau_{HB}$), which usually follows an Arrhenius law

$$\tau_{HB} = \tau_0 \exp\left(\frac{E_{act}}{K_B T}\right),$$

where $E_{act}$ is the energy required to break the HB. Inelastic UV (IUVS) and X-ray (IXS) Brillouin Scattering have proved to be valid tools to determine $\tau_{HB}$ through the so-called structural relaxation time ($\tau_\alpha$), which can be determined in water and in several other (HB and non-HB) liquids. The characteristic timescale for $\tau_\alpha$ in fact (i.e., $\tau_\alpha = 0.1-10$ ps in liquids) matches with the average timescale for the intermolecular bonds lifetime. However the so obtained $\tau_\alpha$ gives information about the average HB behavior, mediated on the whole species of HB present in the solution.

We have investigated, by means of UV Brillouin and Raman spectroscopes, the behavior of glycine aqueous solutions as a function of temperature and concentration to shed light on the temperature behavior of the glycine hydration shell. The presence of a crossover temperature at $= 60^\circ$C, above of that the hydration shell breaks down has been identified. Furthermore, through a careful Raman spectra lineshape analysis of we were able to determined the strength of a single hydrogen bond species present in the solution.

![Figure 1. Temperature and concentration behavior of $\tau_\alpha$ in several glycine aqueous solutions at different concentrations. Reprinted with permission from DOI: 10.1063/1.4812283. Copyright 2013, AIP Publishing LLC.](image)
in the solution, and cannot be used to identify the behavior of a single HB. However we have recently demonstrated how the correlation time ($\tau_c$) derived by an appropriate lineshape analysis of the isotropic Raman spectrum can be strictly identified with the HB relaxation time $\tau_{\text{rel}}$. If a given atom of an organic molecule (in aqueous solution) forms HB's with the surrounding molecules, then the activation energy of those HB can be extracted through an Arrhenius fit of $\tau_c(T)$, as determined by the analysis of the Raman peaks associated with the involved atoms and functional group. We have therefore realized a pilot experiment using a simplified system (glycine aqueous solution) with the aim of measure the HB between water and the hydrophilic part of glycine and to characterize the behavior of the glycine hydration shell. As a first we have calculated the $\tau_c$ trend in several glycine aqueous solutions as a function of temperature and concentration ($n$ is the ratio between water and glycine molecules). The values are plotted in Fig. 1. It is clearly evident a rise in the relaxation time occurring at temperatures lower than $\approx 60^\circ$C (red arrow in Fig. 1) in the glycine solutions. Such behavior can be explain considering that the HB involving the water molecules surrounding the hydrophobic groups are stiffer than the bulk water ones. Instead in Fig. 2 is shown the temperature behavior of $\tau_c$, as derived from the Raman lineshape analysis of the glycine C-O symmetric stretching. The O atoms of glycine forms HB with water molecules, therefore the activation energy derived from $\tau_c$ can be considered as an estimation of HB free energy. No discontinuities can be shown near $\approx 60^\circ$C in the $\tau_c$ trend, demonstrating how the observed discontinuity of $\tau_c$ in Fig. 1 can be only ascribe to the behavior of the hydrophobic groups. Concluding, by means of Raman spectroscapes we were able to determine the strength of a single HB species. At the same time, comparing Brillouin and Raman results, we have described the temperature behavior of the glycine hydration shell. We believe that the proposed approach can be used also to investigate the HB thermodynamic behavior in more complex biomolecules.

Figure 2. Temperature behaviour of $\tau_c$ derived from the C-O stretching isotropic Raman peak, obtained from $n=30$ glycine aqueous solution. Reprinted with permission from DOI: 10.1063/1.4812283. Copyright 2013, AIP Publishing LLC.
Nature is a school for nanomagnetism, many organisms are able to produce magnetic nanoparticles with properties superior to those of similar synthetic materials. Magnetotactic bacteria are a good example of this. These bacteria biomineralize magnetite nanoparticles surrounded by a lipid bilayer membrane, called magnetosomes. The magnetosomes are organized in chains and are used as a compass needle to orient and navigate along the geomagnetic field lines.

The good biocompatibility of the magnetosomes, together with their high structural and chemical quality, has attracted great interest from the scientific community, especially in the field of biomedical applications. A good understanding of the biomineralization of the magnetosomes is the key to design new materials and applications. In general, little is known about the biomineralization process, and in the last years different models have been proposed regarding how the Fe, taken up from the medium, precipitates in the form of magnetite nanoparticles. In order to shed light on this topic, we have studied the biomineralization process of the magnetotactic bacterium *Magnetospirillum gryphiswaldense* strain MSR-1 by the combination of magnetic and structural techniques in a time-resolved study. With this aim, nonmagnetic cells were grown in an iron free medium. Afterwards, to induce the magnetite biomineralization, these iron starved cultures were harvested by centrifugation and the cells were transferred to fresh medium supplemented with Fe(III)-citrate. At specific time intervals from $t = 20$ to $360$ min, the cells were collected and fixed in formaldehyde for transmission electron microscopy (TEM) imaging, magnetic characterization, x ray absorption near edge structure (XANES), and high resolution TEM (HRTEM).

*Figure 1.* Magnetosomes and chain formation followed by TEM together with the corresponding size-distribution histograms. Reprinted with permission from *ACS Nano* 7 (4), 3297–3305 (2013), Copyright (2013) American Chemical Society.
with increasing time, the number and size of the nanoparticles increases, and they form small sub-chains. After 240 min, full chains composed of 45 nm sized particles are observed. These particles are cubo-octahedral, and HRTEM microdiffraction confirms that they are pure monocrystalline magnetite.

The same bacterial samples were analyzed by XANES. Experiments were performed at room temperature and both, transmission and fluorescence signals, were recorded simultaneously. XANES is an element specific technique very sensitive to the local structure and oxidation state of the absorbing element. Therefore, XANES is an ideal technique not only to identify but also to quantify the different Fe inorganic phases present in the bacteria. We found that the energy edge of the spectra shifts 2 eV to lower energies from the beginning to the end of the biomineralization process, indicating a reduction of Fe (Fig. 2a). Further analysis of the XANES spectra by means of linear combination fits to several iron oxides and hydro-oxides show that only two Fe phases are involved in the biomineralization process, namely ferrihydrite (Fe$^{3+}$) and magnetite (Fe$^{3+,2+}$). The origin of the ferrihydrite could be at bacterial ferritin cores, owing to their similar XANES spectra characterized by a poorly crystalline structure and high phosphorus content. From the combination of the XANES and magnetic results, we have been able to quantify the mass of Fe per cell in each phase at every time after Fe induction (Fig. 2b). These results show that in the first stages of the biomineralization process the mass of ferrihydrite per cell remains almost constant, suggesting that the accumulation of Fe in the form of ferrihydrite prevails over the biomineralization of magnetite. In a second step, the magnetite is rapidly biomineralized from ferrihydrite, the mass of which decreases slowly until it becomes undetectable.

**Figure 2.** a) Fe K-edge XANES spectra at specific times after Fe incubation, and the corresponding fit. b) Mass distribution of Fe per cell in the magnetite and bacterial ferrihydrite phases as determined by the combination of magnetic and XANES results. Reprinted with permission from *ACS Nano* 7 (4), 3297–3305 (2013), Copyright (2013) American Chemical Society.

**Original Paper**

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A Platelet Rich Plasma (PRP) Based Membrane Periosteal Substitute: a New Concept for Bone Repair

The periosteum plays a pivotal role during bone repair contributing to bone vascularization and as an osteoprogenitor cell source. We proposed a periosteal substitute engineered using a platelet rich plasma membrane incorporating bone marrow mesenchymal stem cells to be wrapped around an osteoconductive scaffold for regeneration of compromised bone defects. The characterization and optimization of the PRP/BMSC gel membrane were performed by in vitro tests and by a rabbit segmental bone defect model we provide evidence of its capacity to biomimic a periosteal response enhancing bone regeneration.

The periosteum, is a microvascularized connective tissue covering the outer surface of cortical bone, with an outer fibrous layer and an inner cambium layer. Periosteal vessels form an extensive meshwork covering the entire length of bone surface, providing osteoblast precursors for new bone formation besides nutrients and oxygen supply. Damage or removal of the periosteum affected osteogenesis and chondrogenesis, decreased neovascularization and resulted in poor remodeling activity and delayed healing. Therefore, designing a functional periosteal substitute that is capable of mimicking a natural periosteal response by both enhancing vascularization and providing essential osteogenic precursors may have substantial implications on the field of bone engineering.

To increase the vascular supply for enhancing bone healing and repair, several approaches have investigated: engineering arterioles and capillaries using synthetic and biological material, implantation of co-cultured osteogenic-angiogenic cells, and local delivery of angiogenic/osteogenic growth factor combinations. In addition, owing to the established part played by the periosteum during bone repair, contemporary studies have attempted to engineer periosteum substitutes to more closely mimic the endogenous repair process and overcome current problems of traditional cell/scaffold based approaches. The periosteum, a microvascularized connective tissue covering the outer surface of cortical bone, with an outer fibrous layer and an inner cambium layer. Periosteal vessels form an extensive meshwork covering the entire length of bone surface, providing osteoblast precursors for new bone formation besides nutrients and oxygen supply. Damage or removal of the periosteum affected osteogenesis and chondrogenesis, decreased neovascularization and resulted in poor remodeling activity and delayed healing. Therefore, designing a functional periosteal substitute that is capable of mimicking a natural periosteal response by both enhancing vascularization and providing essential osteogenic precursors may have substantial implications on the field of bone engineering.

Given its indispensability for bone regeneration and revascularization, we aimed to engineer a biomimetic periosteal substitute to envelope an osteoconductive scaffold for regeneration of critical size segmental bone defects. In our construct, bone marrow derived progenitor/stem cells (BMSC), as the osteoinductive components, were entrapped within a platelet-rich plasma (PRP) gel membrane. PRP is a platelet enriched plasma that enhances tissue repair thanks to the mitogenic, angiogenic and chemotactic factors released by the platelets in the wound site which induce cell migration, proliferation and differentiation. In our study, the PRP gel membrane derived from the gelification of PRP and Cryoprecipitate (fibrinogen enriched plasma) in the presence of Thrombin and Calcium Gluconate. The components were mixed in a standardized proportion in order to get a high platelet derived growth factor concentration. The PRP gel membrane was able to support cell viability and proliferative capacity.

The functionality of the PRP/BMSC gel membrane was also tested to verify its angiogenic properties through an in vitro migration assay which showed that endothelial cells migrated in response to factors released by the membrane reflecting an angiogenic capacity. The functionality of the PRP/BMSC gel membrane was also
tested in a critical size bone defect surgically created in the rabbit ulna. A nanohydroxyapatite/polyester urethane cylindrical scaffold was selected as the scaffold of choice. In the study the animals were divided into three groups: scaffold alone (control, GROUP A); scaffold loaded with BMSC (GROUP B) and scaffold wrapped with the PRP/BMSC gel membrane (GROUP C). The animals were monitored through radiographic controls and at the end of the study Transmission x-ray computed microtomography (µCT) was performed using a microfocus x-ray source with cone beam geometry at the TOMOLAB station (www.elettra.trieste.it/Labs/TOMOLAB). Both radiographic and µCT images revealed that group (A) defects treated with scaffold alone showed no new bone formation (Fig. 1A). Group (B) defects treated with scaffolds loaded with autologous BMSC showed limited bone formation at the distal and proximal ends of the defect with small islands of bone developing within the scaffold close to the periphery (Fig. 1B). Group (C) defects treated with scaffolds wrapped with the PRP/autologous BMSC gel membrane showed the greatest amount of bone regeneration in the defect area with the formation of new bone attempting to bridge the defect area traversing peripherally where the PRP/BMSC gel membrane was implanted (Fig. 1C). Rabbit ulnas were also analyzed by histological analysis showing absence of bone formation in the control group (GROUP A), limited bone deposition in GROUP B while GROUP C showed mature bone formation and development of vascular structures. In conclusion, in this study we engineered and characterized a PRP gel membrane entrapping BMSC that could mimic the natural periosteum in supporting bone regeneration including the definition of a standardized platelet derived membrane that creates a favorable angiogenic and osteogenic microenvironment for enhancing bone tissue repair.

Figure (A, B, C): Four month post-operative radiographs (left) and µCT of rabbit ulna defects filled with (A) Nanohydroxyapatite/ poly(ester urethane) scaffold with PBS; (B) Nanohydroxyapatite/ poly(ester urethane) scaffold seeded with autologous rBMSC; (C) Nanohydroxyapatite/ poly(ester urethane) wrapped with PRP/rBMSC gel membrane. Images are representative for one rabbit from each group. (D, E, F): Low power reconstructions of overall histological appearance of segmental rabbit bone defects after 4 months for groups (A), (B) and (C) in D, E, and F, respectively with an adjacent diagrammatic sketch of the defect and the treatment received. Bar= 5mm. Reprinted with permission from DOI:10.1089/ten.tea.2012.0357.

Original Paper
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Ptychography can retrieve the modulus and phase of both the sample transmission function and the illuminating probe from diffraction data. Ptychographic reconstructions at x-ray energies around the L absorption edge of iron gave amplitude and phase contrast images of cobalt ferrite nanoparticle clusters, and showed that the phase variations across the edge can be measured simultaneously, and in perfect registration with, conventional NEXAFS mapping. A random array of nano-scale pinholes was used to spread the signal across the detector plane, better matching the dynamic range of the detector.

Ptychography has become an important imaging tool in x-ray microscopy. It involves successively illuminating overlapping regions of a specimen with a coherent x-ray probe and recording the resulting diffraction patterns. The illuminated areas must overlap significantly, since the common areas provide duplicate information that allows computer algorithms to reconstruct reliably both the complex sample transmission function and the complex amplitude of the illuminating probe from the measured diffraction data. The study reported here demonstrates its application in the soft x-ray regime, at energies around 700 eV. The illuminating probe was defined by a 5 µm pinhole located about 1.25 mm upstream of the sample, as shown in Fig. 1. In the experiments carried out on the TwinMic beamline at Elettra, a random array of 40 nm diameter pinholes etched into a thin tungsten film was placed about 1.5 mm upstream of the beam-defining pinhole to act as a diffuser, reducing the dynamic range of the recorded diffraction patterns by about an order of magnitude and better matching the response of the detector. The sample was scanned in small rectangular rasters perpendicular to the beam direction, with raster steps ~1 µm to ensure significant overlap between adjacent illuminated areas.

The ptychographic method described above was used to image Balb/3T3 mouse fibroblast cells that had been exposed to cobalt ferrite (CoFe₂O₄) nanoparticles. The ePIE (extended Ptychographic Iterative Engine) algorithm developed at Sheffield University, UK, was used to generate a number of ptychographic reconstructions at a range of x-ray energies around the iron L absorption edge. The modulus (amplitude) and phase contrast from clusters of the nanoparticles varied quite strongly as the incident x-ray energy was increased.

Figure 1. Schematic representation of the experimental setup on the TwinMic beamline. A monochromatic x-ray beam illuminates a random array of holes (~40 nm diameter) which act as a set of randomly phased point sources, producing a diffuse beam that illuminates the 5 µm diameter pinhole. The sample is scanned across the beam in a small raster, and the CCD normally used for full-field imaging records the diffraction pattern produced by the sample for every position in the raster scan. Adapted with permission from DOI:10.1038/ncomms2640. Copyright 2013 Nature Publishing Group.
The two signals can be related directly to the optical thickness \((n-1)t\) where \(t\) is the thickness of the cluster and \(n=1-\delta-i\beta\) is the complex refractive index of the material. In practice, five different classes of behaviour across the iron L\(_3\) edge were identified, as shown by the colour coding of the graph in Fig. 2, indicating that the iron present in the nanoparticle clusters was in a number of different chemical states.

The observed variations in modulus contrast across the iron L\(_3\) edge are consistent with estimates based on total electron yield (TEY) measurements made by Dr V.S. Coker of Manchester University, UK. However, the use of ptychography to recover the complex sample transmittance has allowed the first direct measurements from cobalt ferrite nanoparticles of the phase variations across the iron L\(_3\) edge, with the phase variations showing stronger and clearer features than the conventional near-edge x-ray absorption fine structure (NEXAFS) measurements. The ptychographic approach offers some important advantages for high-resolution x-ray spectromicroscopy. It provides a spatial resolution which is comparable to that achieved when the TwinMic microscope is operated as a conventional scanning transmission x-ray microscope (STXM), while the use of a relatively large probe allows an extended area of the sample to be covered in a raster of modest size, with no refocusing required when the incident x-ray energy is changed. The ability of x-ray ptychography to provide direct, quantitative phase information, in perfect registration with conventional NEXAFS data, should open up a rich new branch of x-ray spectromicroscopy.

Figure 2. (a) Plot of the \(\log_e(\text{modulus})\) and phase image signals measured from the CoFe\(_2\)O\(_4\) nanoparticles. The locations of the nanoparticle clusters are highlighted by coloured dots in the inset image (phase image at 711.8 eV). The curves show that five different classes of behaviour as a function of x-ray energy were identified. For comparison, a scaled plot of the TEY signal from similar particles is overlaid on the \(\log_e(\text{modulus})\) plots. The solid and dashed black lines show the signals calculated for a 90-nm thick film of CoFe\(_2\)O\(_4\) derived from the semi-empirical tabulation of atomic scattering factors by Chantler et al. (http://www.nist.gov/pml/data/ffast/). (b) Reconstructed modulus and phase images of a Balb/3T3 mouse fibroblast. The data were collected at x-ray beam energies across the iron L edge, showing the variation in contrast of the CoFe\(_2\)O\(_4\) nanoparticles as a function of energy. Scale bar, 5 µm. Adapted with permission from DOI:10.1038/ncomms2640. Copyright 2013 Nature Publishing Group.

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Original Paper
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Unzipping dsDNA confined monolayers: RecQ and RecQ1 helicases

We investigated the unwinding kinetics of two helicases, *E. Coli* RecQ and its human homologous RecQ1, in vitro, within dense dsDNA monolayers realized by means of Atomic Force Microscopy nanografting. Exploiting the different mechanical properties of ss and dsDNA and monitoring with high precision the changes in height due to the separation of the strands carried out by the enzyme, we measured the reaction kinetics of the two enzymes. By using this assay we estimated the unwinding rate of the RecQ1 helicase, and explained its reduced rate when compared with the bacterial homologous helicase.

Strand separation in DNA is a crucial step for cell replication. Among the proteins involved in the replication machinery, helicases are the enzymes responsible for the opening of duplexes, in many cellular processes. In particular, the RecQ family is mainly involved in genomic maintenance. In humans there are five helicases belonging to the RecQ family: RecQ1, BLM, WRN, RecQ4 and RecQ5. Despite the high abundance in human cells and its putative role in cancer, RecQ1 has been less studied with respect to the other RecQ helicases. In particular its function and its unwinding mechanism are still debated in literature. In order to elucidate the mechanisms of action and the reaction kinetics of RecQ1 we monitor the unwinding of double stranded (ds)DNA molecules anchored on a solid substrate by means of Atomic Force Microscopy topographic measurements, comparing the observed behavior with the one of the bacterial homologous RecQ. We immobilize thiolated dsDNA forked substrates (42 base pairs long) in micrometer sized assemblies by means of AFM Nanografting, a lithographic technique that allows for

substitutional adsorption of molecules on a gold surface. When the enzyme acts on the duplex, it releases in solution one strand leaving on the surface only the single stranded (ss)DNA anchored via thiol-gold bond. Since the mechanical properties of ssDNA and dsDNA are dramatically different (the persistence length of ssDNA is about 50 times smaller then the one of dsDNA) their response to the applied load of the tip of the AFM (approximately 0.1 nN) will result in a consistent decrease in the measured height after unwinding. We follow then the topographic height variation of the dsDNA assembly as a function of enzyme incubation time, until we reach the complete unwinding of the DNA substrate.

![Image](https://example.com/image1.png)

Figure 1. Schematics of the helicase unwinding assay and AFM images and corresponding average line profiles of a dsDNA patch after incubation with RecQ1 at different reaction time. Adapted with permission from DOI:10.1021/jz3018682. Copyright 2013 American Chemical Society.
In Fig. 1 we report the experimental setup and AFM images corresponding to different incubation time. We start with a dsDNA confined monolayer, we acquire a topographic image of the DNA assembly and we measure the height ($\Delta h_0$) of the structure relative to the surrounding biorepellent self assembled monolayer. Then we let the enzyme work for a certain amount of time $t_1$ and acquire a new topographic image of the samples, recording the new relative height ($\Delta h_1$). We repeat this process for different incubation time. A plot of the evolution of the height variation vs. reaction time is shown in Fig. 2. Assuming that the height variation scales linearly with the number of dehybridized molecules in the patch, we can calculate the estimated fraction of unwound substrate as a function of time. Then using a two steps model (non productive binding of the enzyme to the DNA and unwinding process), we can fit our data with an analytic expression describing the time-dependent formation of the fraction of unwound ssDNA molecules. From the fit we found an unwinding rate of $0.24 \pm 0.04$ bp s$^{-1}$ and $0.036 \pm 0.008$ bp s$^{-1}$ for the bacterial RecQ and for RecQ1, respectively. The ~10 time slower unwinding activity of the human RecQ1 with respect to its bacterial homologue RecQ can be explained taking into account different aspects. First, with respect to its bacterial homologous, RecQ1 lacks the C-terminal part that is thought to be responsible for the binding to the DNA substrate. The reduced binding affinity of RecQ1 can slow down the reaction. Moreover RecQ1 is known to act as a dimer, whereas the RecQ prevalently acts as a monomer. Due to sterical hindrance, the slippage of the dimer through the DNA monolayer is expected to be less efficient, resulting in a reduced processivity. Our assay allowed a first estimation of the unwinding rate for the RecQ1 on surface immobilized DNA and highlighted the different processivity behavior with respect to E. coli RecQ. Further studies on substrate specificity, sequence length and ATP concentration will provide a better understanding of the unzipping mechanism.

Figure 2. Average height variation of different DNA patches as a function of the incubation time of human RECQ1 (blue dots). The dashed lines represent the height of the initial ssDNA patches (red) and the height of the self assembled monolayer of the alkanethiol Top terminated with 6 units of Ethylene Glycol (TOEG6) used as reference (green). Adapted with permission from DOI:10.1021/jz3018682. Copyright 2013 American Chemical Society.

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Original Paper
Asbestos is a potent carcinogen associated with malignant mesothelioma and lung cancer but its carcinogenic mechanisms are still poorly understood. Asbestos toxicity is ascribed to its particular physico-chemical characteristics, one of them is the presence and ability to adsorb iron, which may cause an alteration of Fe homeostasis in the tissue. In our study, a combination of advanced synchrotron-based x-ray imaging and micro-spectroscopic methods provided correlative morphological and chemical information to shed light on Fe mobilization features during asbestos permanence in lung tissue.

Asbestos is a fibrous silicate with particular physical/chemical properties and tensile strength that makes it an ideal material for various construction and covering purposes. For this reason it was widely used for more than 100 years and is currently still used in some countries, despite the alarming reports about its toxicity and carcinogenicity. Today it is definitely demonstrated that asbestos exposure is associated with development of pulmonary diseases including bronchogenic carcinoma, mesothelioma, pleural plaque and asbestosis. While asbestos toxicity is undeniable, the exact pathogenic mechanisms by which asbestos fibres trigger pulmonary toxicity and neoplastic transformation have not been fully understood. Most often, the toxicity is ascribed to the specific physico-chemical characteristics of asbestos and, in particular, to its ability to adsorb iron that may cause an alteration of iron homeostasis in the tissue. When asbestos fibres are inhaled, they may get trapped into the lung and remain all life long in the body locked inside biostuctures called “asbestos bodies” and constituted by fibres coated by high quantities of iron containing proteins. Using a combination of advanced synchrotron-based x-ray imaging and micro-spectroscopic methods we studied representative tissue samples from ten patients exposed to asbestos (from shipyard workers in Monfalcone) obtaining important correlative morphological and chemical information for the chemistry of asbestos body formation and other changes in the surrounding lung tissue that cannot be obtained using conventional techniques. The iron concentration, distribution and speciation in diseased human lungs, monitored for the first time thanks to the high elemental and chemical sensitivity of synchrotron XRF spectro-imaging and micro-XANES, have shed light on the iron mobilization during asbestos permanence in lung tissue. The Fe XRF maps (Fig. 1) clearly demonstrate how the asbestos fibres and the formed iron-rich bodies around them can cause high mobilization of iron into the surrounding cells (mainly alveolar macrophages) and tissue. The results suggest both, continuous deposition of Fe-containing species (ferritin) around the asbestos fibres and metal release...
due to asbestos body degradation. As already reported in previous studies, along with iron other chemical elements participating in the formation of asbestos bodies are phosphorus, calcium and magnesium indicative for calcification process as well. Comparing the Fe and Ca maps (Fig. 1) it is evident that Ca concentration in the body and in the vicinity is more evenly distributed, which is most likely a consequence of phagocytosis.

Here and in a previous study conducted at the TwinMic beamline of Elettra we have also demonstrated the presence of magnesium in the asbestos bodies and its surroundings has been demonstrated too. This indicates that, along with adsorption of iron-containing species, the first steps of interaction between the asbestos fibres and the tissue involve magnesium aggregation. (Fig. 2) In the following stages the bio-mineralization process continues most likely inside the macrophages, involving ferritin together with phosphate, calcium and magnesium.

Since the oxidation state of Fe could provides important information on the processes involved in the asbestos body formation, Fe K-edge XANES were measured in selected ~ 1 µm² spots from the Fe maps at the ID21 beamline of ESRF synchrotron. The means confirm that most of the iron detected around asbestos fibres (coating and ferruginous bodies) is compatible with the presence of ferritin and the Fe3+ oxidation state of iron. In addition, XANES analyses demonstrate to be useful to potentially discriminate in lung tissues the fate of iron-containing fibres from iron-free asbestos. However the most novel and intriguing result of XANES analyses was the detection of significant percentages of haematite in the asbestos bodies that we suppose is the results of ferritin transformation occurring during the long residence time in the asbestos bodies in the lung tissues.

Figure 2. Micro-XANES analyses on asbestos bodies. An example of a deconvoluted micro-XANES spectrum of an asbestos body measured with a microprobe of 1 µm². Adapted with permission from DOI:10.1038/srep01123. Copyright 2013 Nature Publishing Group.
Oleic and elaidic acids are the two most abundant fatty acids in food products and vegetable oils. Synchrotron high resolution Small and Wide Angle X-ray Scattering (SAXS/WAXS) investigations were performed to study their influence on a monoglyceride membrane structure. Exploring the effect of these two fatty acids on biological membrane structures is of great interest due to the implications of their daily consumption in vital biological processes related to health and disease, and their role in designing gel-like formulations for controlling the release of drugs or functional foods.

The traditional Mediterranean diet supplemented with olive oil is associated with beneficial health effects. In European countries such as Greece and Italy and in the Middle East the intake of olive oil is high and is linked in different regions to a relatively reduced blood pressure and a reduced risk of developing coronary heart disease, a reduced breast cancer, and a low level of plasma cholesterol. Various studies suggested that the consumption of olive oil, which is rich in oleic acid (monounsaturated fatty acid with the natural cis configuration), is strongly associated with positive health effects. This explains the interest in recent years in introducing to the market new food products with low and even zero trans fatty acids content. A first positive trend has been set by the food industry, e.g., in the UK, where according the latest National Diet and Nutrition Survey (2011) the trans fatty acids are now only found at low levels in foods indicating that average trans fats intake was less than 2 gr. per day for all age groups, which falls below the maximum WHO recommendations.

In contrast to the traditional Mediterranean diet, different industrial food products in the market are rich with trans fatty acids (unsaturated fatty acids with the non-natural trans configuration), which are produced during the well-known process of partial hydrogenation of unsaturated oils in food industry, and their dietary is associated with various negative health effects including an increased risk of coronary heart disease and cancer, and increase in body weight. This explains the growing interest in introducing to the market new food products with low and even zero trans fatty acids content. A first positive trend has been set by the food industry, e.g., in the UK, where according the latest National Diet and Nutrition Survey (2011) the trans fatty acids are now only found at low levels in foods indicating that average trans fats intake was less than 2 gr. per day for all age groups, which falls below the maximum WHO recommendations.
In this study, synchrotron SAXS was applied for studying the effect of two of the most abundant fatty acids in cis (oleic acid) and trans (elaidic acid) fat dietary intake on the structure at the nanoscale level of monoglycerides, which are unique lipids displaying a rich variety of structures at different water content and temperatures. The monoglycerides are ingredients in different food products and are interesting as they form biologically relevant intermediates during fat digestion and metabolism. Noteworthy, the difference in the molecular shape of the investigated fatty acids (elaidic acid has a rod-like molecular structure; whereas oleic acid has a more cone-like shape) has a significant impact on the lipid structuring. The experimental findings show that both fatty acids lead to a variety of diverse structures when mixed with the monoglyceride monoelaidin in the presence of excess water (monoelaidin is a lipid derived from elaidic acid). The phase transition boundaries and stability can be easily controlled by the amount of the added fatty acid and by changing the temperature. Clearly, oleic acid due to its cone-like molecular structure induces stronger interfacial membrane curvature as compared to elaidic acid, and provides the membrane with a higher flexibility. Our results are in a good agreement with previous studies suggesting that oleic acid is more efficient than elaidic acid in modifying the properties of lipid membranes. For instance, it was suggested that the reduction in the blood pressure is linked to the membrane structure that can be modified by oleic acid to regulate the biological activity.

Fig. 1 shows an example on the effect of oleic acid on controlling the nanostructure of monoelaidin in the presence of excess water. The effect of adjusting the loaded amounts of oleic and elaidic acids on the temperature-dependent structural behaviour of monoelaidin in the presence of excess water is illustrated in Fig. 2. It is fascinating to obtain these unique tuneable structures by rather simple means and to highlight the role of oleic and elaidic acids on model membrane structuring.

Original Paper

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ELETTRA status report

After three years of successful operations in the top-up mode at both 2 and 2.4 GeV ring energies efforts continue towards increasing the availability reproducibility and stability of Elettra. We report here on the current status and recent improvements of the Elettra storage ring and its injectors, providing also the machine up-time statistics.

Elettra constantly operates in top-up mode, where frequent and fast injections with the shutters open maintain the accumulated beam current almost constant, allowing users to acquire data without any major interruption due to the ring refilling. In addition, owing to the top-up, the machine has achieved higher stability and reliability. Due to the high efficiency of the injections, the radiation levels in all beamlines remain below 1 mSv/h for both 2.0 and 2.4 GeV ring energies. With 310 (170) mA ring current at 2 (2.4) GeV, top-up is repeated every 6 (20) minutes by injecting a current of 1 mA in 4 s, keeping the accumulated current constant within 3‰ (7‰). Disturbance to data collection is minimal, with only two beamlines using the provided gating signal to interrupt acquisition during injections. In parallel in order to further improve the availability, stability and reproducibility, staying thus competitive to the most recent machines, a series of small but important projects are under way. Briefly are mentioned the ambient temperature stabilisation to ±0.5 C, the continuing installations of additional correctors to render the dipole beam lines source point independent from that of the straight sections beam lines, the tests with the digital low level rf prototype that will allow a higher

![Availability on scheduled user beam time](image)

**Figure 1.** Availability of Elettra since 2004.
radiofrequency stability of the beam, the series production of the power supply modules of the booster main magnets, the beam dump fast diagnostics that will help in understanding the source of beam dump in real time and thus reducing the debugging and intervention time, the upgrades of the power supplies control system, the replacement of a second rf klystron plant with one using IOTs and in parallel a development plan for a solid state rf amplifier and the photon beam position monitors in test. In addition to all that the refurbished super conducting wiggler has been installed in the ring, ready to operate (see next article).

The injector: the injection chain main components are a 100 MeV linear accelerator and a 2.5 GeV 3 Hz booster. During the last year our efforts to improve the linear accelerator were focused on eliminating the klystron discharges that however did not pose any problem on the reliability of the linac. Currently one discharge every 2.5 days has been achieved. Although Elettra operates at 2 and 2.4 GeV for the General Users, the booster can provide any energy from 0.1 to 2.5 GeV or even higher. The rebuilding of the modules of the digital power supplies is continuing, all big booster power supplies now run on the in-house made modules. The percentage of top-up compared to total beam time delivered to the users is a good measure of the availability of the injector, which, for 2013, is at 97.84% at the time of writing while the machine downtime due to injectors is 0%.

The Storage ring: the users work mainly with multi-bunch filling. This means that a large portion (typically 90 to 95%) of the 259.2 m circumference of the ring is filled with electrons letting only a small gap for ion cleaning. In 2013 the hybrid mode has also been requested and amounted so far to 13% of the user time at 2 GeV and 31% at 2.4 GeV. In the hybrid mode a single bunch of about 5mA is injected in the centre of the empty space in the storage ring filling allowing the users to exploit the pulsed nature of synchrotron radiation in time resolved experiments. The hybrid procedure is now fully supported in top-up. Since the beginning of the Elettra upgrade there were high expectations that top-up would improve the availability of the machine. In Fig. 1 one can see the availability during the 3 phases of operations of Elettra. Before 2008 the storage ring was used with energy ramping, whereas since 2008 it operated with a full energy injector. Since 2010 the machine is functioning in top-up mode and a clear improvement can be seen. Another important parameter describing the reliability of a light source is the mean time between failures (MTBF), i.e. the average time the machine runs without interruption. Also in this case (see Fig. 2) a clear improvement can be observed after 2008. In 2013 the MTBF so far is 55 hours (77 hours if excluding storms). In 2013, the average longest duration of top-up operation without failures was 300 hours and excluding beam dumps due to storms this figure is 400 hours. The electron orbit stability is also excellent. The long term (140 to 260 hours) peak-to-peak orbit stability is within 10µm and 8 µm in the horizontal and vertical plane, respectively, whereas the short term (8-24 hours) values approach 1.7 µm in the horizontal and 0.3 µm in the vertical plane. This corresponds to 0.9 µm in the horizontal and 0.3 µm in the vertical plane rms stability. A beam orbit stability of better than 2% of the rms beam size is a much better figure than the usually requested 10% in the specifications. These results are achieved only if the cooling water and ambient temperature stay as specified by design requirements. The orbit was found to be affected by the thermal stability of the machine. When re-injecting from empty to operating current after a beam dump, the time required for the machine to reach thermal equilibrium, and therefore also for the orbit to get back to its normal position, is almost 1.5 hours.

![Figure 2. Mean time between beam losses since 2004.](image-url)
The renewed superconducting wiggler: a potent hard x-ray source serving three beam lines

The description and status of the refurbished superconducting wiggler is presented together with its new improved features.

Introduction: The superconducting wiggler (SCW) was ordered from Budker Institute of Novosibirsk (BINP) in 2000 and installed in the Elettra storage ring in 2002 as a high intensity source in the hard x-ray region. It has a period length of 64 mm for 24.5 periods (49 poles) reaching 3.5 T with an output power of 18 kW at 2 GeV and 400 mA. Its critical energy at 2 (2.4) GeV is 9.3 (13.4) keV while its brilliance stays almost constant, in the order of $10^{15}$ photons/sec/mm²/rad²/0.1%bw up to 30 keV at 2.4 GeV (Fig. 1), to be used for beam lines requiring hard x-rays mainly in crystallography. However due to lack of funds for the dedicated beam-line, and although already installed in the storage ring and successfully commissioned [1], it remained unused with zero field. Lately, with the agreement of a collaboration with the Indian government for 2 beam lines (XRD2, XPRESS) and with the open possibility of a third line for pharmaceutical research, funds were found and the wiggler had to operate. Tests made in 2011 to control its functional status revealed however that after so many years of disuse the magnetic field could not go beyond 0.9 T while in parallel they showed an anomalous liquid He (LHe) consumption up to 7 L/h probably due to ice formation inside the magnet. Nevertheless, even the nominal consumption of 0.5 L/h as measured in [1] was absolutely incompatible with the new operating mode of Elettra.

Figure 1. The SCW brilliance (photons/sec/mm²/rad²/0.1%bw) for the two operational energies of Elettra @ 100 mA. For comparison the brilliance from the bending magnet is also shown.

Figure 2. LHe consumption during a 76 hours test at fields from 3.2 to 3.6 T.
namely the top-up. Indeed that consumption (about 0.5 L/h) means that the beam should be dumped every two - three weeks in order to replace the lost LHe, not to mention also its high purchase price. It was therefore decided to send the SCW to BINP in order to have its magnet repaired and its cryostat refurbished to obtain a zero liquid He consumption.

Construction, installation and operation:
In 2011 the project and its technical specifications were defined and the order for the SCW refurbishing was placed. The wiggler was taken from the storage ring in January 2012 while in March the project acceptance meeting took place. The FAT was successfully concluded at BINP in April 2013 and the SCW arrived in Elettra in June 2013. After successfully completing the SAT with only two quenches both occurring at a field higher than the 3.5 T nominal, and controlling the He consumption without beam (see Fig 2), in July 2013 the SCW was installed in the storage ring (see Fig 3 ) and was tested with a beam of 80 mA at 3.5 T. Due to front-end degassing it had not been possible until then to test the wiggler at full beam intensity (310 mA at 2 GeV or 170 mA at 2.4 GeV). Currently, for conditioning and alignment reasons the wiggler is set to 0.5 T at both operating energies of Elettra during user shifts while its LHe consumption to date is zero. No particular operational problems were encountered and it has been planned to gradually increase the magnetic field in order to have the wiggler at 3.5 T during user shifts in December 2013.


Figure 3. The refurbished superconducting wiggler installed in section 11
FERMI
FERMI welcomed its first external users in December 2012. The first user run lasted until beginning of April 2013 and was very successful with pump-probe experiments performed for the first time at FERMI. During the spring shutdown the 50 Hz upgrade of various systems was completed and in May the commissioning of the linac at 50 Hz repetition rate started, along with the linac energy increase to 1.5 GeV. The FEL-2 commissioning has continued by gradually increasing the electron beam energy to push the wavelengths of the photons towards the lower limit. In June 2013 the FEL lased at 4.08 nm.

Between December 3rd, 2012 and March 6th, 2013 FERMI welcomed the first external users, selected via the first call for proposals. 1120 hours of beamtime on the FEL-1 beamline were provided to 12 different experiments on the three experimental stations (DIProl, LDM and EIS-TIMEX). The global machine uptime was good, at 85%. Wavelength ranges between 65 nm and 20 nm were provided. FEL tunability and variable polarization were extensively used. The feedback from the users is positive; many of them indeed expressed their satisfaction for the excellent performance of the FEL and for the high quality experiments they could perform. In December, two colour experiments were performed by using a double seed laser pulse to generate two FEL pulses separated by up to 800 fs. In this case the FEL provides both the pump and the probe. Furthermore, in February a portion of the seed laser was made available in the experimental hall as an infrared user laser for pump-probe experiments. In Figure 1 shows the first pump-probe experiment performed to find the temporal synchronization between the FEL pulse and the infrared laser on DIProl experimental station. Thanks to this scheme extremely low jitter values between the infrared laser and the FEL have been measured, as low as 10 fs RMS which is a factor of 3 better than the best value reported in literature for other facilities. Double stage cascade lasing on FEL-2 was successfully demonstrated in October 2013, by using the fresh bunch technique, at both 14.4 and 10.8 nm wavelength, with the electron beam energy at 1.0 GeV. This was the first experimental demonstration of a seeded free electron laser configured as a two stages cascade operating in the “fresh bunch injection” mode, where the second stage is seeded by the light produced in the first stage. The commissioning of FEL-2 continued in March 2013, when the electron beam energy

![Figure 1. FEL induced change of optical reflectivity on GaAs. The drop of optical signal is used to find the temporal synchronization between the FEL pulse and the user laser during the pump and probe experiments. In the inset the spatial overlap between the two beams is shown.](image)
was increased to 1.2 GeV to lase at shorter wavelengths, i.e. 5 nm. Later in June, the electron beam energy was increased to 1.4 GeV and the wavelength of FEL-2 could be extended down to 4 nm and below, demonstrating that an externally seeded FEL is capable of reaching the soft x ray range of the spectrum. FEL spectra at the central wavelength of 4.09 nm, with pulse energy of the order of 1 μJ, were measured.

To access the lower wavelengths of the FEL-2 range, it is necessary to increase the linac energy from the 1.2 GeV available until March up to 1.5 GeV. The linac energy was increased by an extensive RF conditioning activity in May, essentially by fully activating the energy doubling cavities (SLED) achieving 1.5 GeV on crest. At the same time the machine repetition rate was increased to 50 Hz; the linac operated at this repetition rate during the RF conditioning, while it was reduced back to 10 Hz for the FEL commissioning, in order to increase the linac reliability for the FEL operation at the higher energy and to reduce some expected cathode aging which was observed on the new 50 Hz photocathode gun. In August, during a second period of RF conditioning, the linac energy attained 1540 MeV on crest and 1500 MeV with the electron beam in FEL operating condition mode, that is with the beam compressed and linearized with the X-band system, which is the nominal electron beam energy for FEL-2 at 4 nm.

During the commissioning period in September, FEL-2 has been further studied and optimized at 7.5 nm; more than 30 μJ of pulse energy could be attained. In this occasion, first test experiments with FEL-2 have been successfully performed on DiProI and LDM experimental stations. Fig. 2 shows a two colour diffraction pattern taken on DiProI during this first test user run. Finally, the second beamtime for users on FERMI will start in October 2013. 45 proposals were submitted to the 2nd call and beamtime has been assigned to 15 of them thanks to their top ranking. Experiments will be performed from October 2013 until July 2014, with FEL-2 commissioning periods in between. In 2014, 4032 hours will be devoted to experiments on FERMI.

Figure 2. Single shot multi-wavelength exposure of a periodic array illuminated by a FERMI FEL-2 pulse. In image a) the diffraction pattern of the first stage of FEL-2 at 37.5 nm is shown on the external part of the CCD plane, while the diffraction peaks close to the centre of the CCD detector are due to the shorter wavelength (7.5 nm) emitted by the second stage. Image b) is a zoom of the central part of the collected diffraction pattern. For both wavelengths the finite dimension of the periodic sample produce interference fringes between successive Bragg peaks (red rectangles), showing a good coherence for both radiations of the source.
In these last years we have witnessed an impressive worldwide growing of the science based on x ray FELs. Although the main scope of these FELs is to overtake intrinsic brightness, coherence and pulse length limits of the synchrotron light, nowadays, the most successful sources are operating in the self-amplified stimulated emission (SASE) mode, therefore with significantly limited wavelength stability and coherence. A pioneering experiment was done at Brookhaven National Laboratories by Yu and coworkers, where a laser-seeded free-electron laser produced amplified, coherent, quasi Fourier transform–limited output radiation at the second harmonic of a CO$_2$ seed laser, with the promise that in the future the x ray spectral range would have been accessible with the same method. The underlying concept, 12 years later, lead indeed to the first lasing of a light source based on the same principle, where the seed itself is generated by a VUV free electron laser. We reported in this contribution the generation of coherent, sub-picosecond soft x ray pulses with variable polarization, generated by the seeded free-electron laser FERMI FEL-2, operating in a two-stage harmonic upshift configuration. It is a double-stage cascaded FEL where the first stage is seeded by the third harmonic of a Ti:Sa laser system or of an OPA continuously tunable laser, and the second stage is seeded by the light produced by the first stage. The FERMI FEL-2 layout is shown in Fig. 1. Initial commissioning experiments in October 2012 with a beam energy of about 1 GeV, were done at an output wavelength of 14.4 nm in planar polarization, with the harmonic conversion to the sixth harmonic (43.3 nm) in the first stage and the third harmonic in the second (i.e., eighteenth harmonic of the seed wavelength). Extensive commissioning continued then at the wavelengths used in the above example in circular polarization, with the final wavelength of 10.8 nm corresponding to the 24$^\text{th}$ harmonic.
of the seed. These tests have both demonstrated that the FEL is capable of producing single-mode narrow bandwidth pulses with energy of several tens of microjoules at these wavelengths. Later on, during run 16 and run 17 (March and June 2013) operating at increased beam energy, 1.2 GeV and 1.4 GeV, the spectral range of operation has been extended down to the water window with an energy per pulse in excess of 1 μJ measured at 4.08 nm. The quality and stability of the FEL spectra is an important aspect of the seeded FEL.

A detailed analysis of the spectral properties of the FEL pulses produced by FERMI FEL-2 has been carried out. As an example we report in Fig. 2 the image of the FEL pulse at 5.4 nm as recorded by the spectrometer CCD. The vertical axis shows the vertical beam size at the spectrometer, while the horizontal axis, where the grating dispersion occurs, shows the spectral distribution of the FEL power. The figure clearly shows that the FEL emission is characterized by excellent spectral line shapes in optimised conditions. Also the transverse profile of the FEL pulses is very close to the $\text{TEM}_{00}$ Gaussian mode. The relative bandwidth measured for this case is $1.7 \times 10^{-4}$ rms that, for Fourier limit pulse, would correspond to a temporal length of about 20 fs (FWHM). Although it has not been measured yet, 20 fs is close to the expected pulse length at such a wavelength due to the pulse shortening occurring in the FEL process. For such a reason we are confident that when the system is properly optimized, the FERMI FEL-2 can produce FEL pulses down to about 5 nm with a very high degree of longitudinal coherence. Our characterisation of the photon pulses prove that a multistage harmonic upshift FEL can operate at high final harmonic number, at the level of the Carbon K-edge, generating close to single transverse mode, narrow spectral bandwidth, soft x ray pulses of several μJ. We expect this FEL configuration to be directly scalable to photon energies in the keV range, in the fundamental or harmonic emission, with a power per pulse that will unlock the gate for experiments in the soft x ray region with femtosecond-variable polarization-Fourier-transform-limited soft x ray pulses.

Figure 2. Single-shot image and spectrum of the FEL intensity with the resonance set at 5.4 nm. The background image shows the intensity as a function of wavelength on the x axis, and vertical size on the y axis. The white line shows the integrated intensity (y axis) versus wavelength (x axis). The bandwidth is about 0.017%.

Original Paper
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The longitudinal electron beam properties are of key importance for frontier accelerators like FERMI. For the online control of the machine, nondestructive shot by shot bunch length measurements are needed. The diagnostics instrumentation based on coherent radiation represent the more robust tools for bunch length control. So far these systems were limited only to provide relative bunch length measurements. We present a novel methodology based on diffraction radiation from a gap and demonstrate its capability to provide an absolute bunch length measurements.

In our paper we presented a novel experimental methodology to self-calibrate a simple device based on diffraction radiation from a ceramic gap. We demonstrate that this provides the absolute measurement of the second order moment of the electron bunch longitudinal distribution (i.e. the bunch length). The method is best suited for measuring bunches with lengths from picoseconds to subpicoseconds, it is independent from other external instruments and the required equipment is extremely simple.

Why coherent radiation?
Incoherent radiation from ultra relativistic particles such as high energy synchrotron radiation from a bending magnet does not contain any information on the bunch as a whole since each electron in the bunch emits incoherently. A short electron bunch can also radiate coherently. This means that all the $N$ electrons in the bunch emit radiation with the same phase, so that the sum of individual electron emission adds up as $N^2$. For hundreds pC bunches, $N$~10 billion electrons, so the coherent emission is very intense compared to incoherent. The spectral content of the coherent radiation of a picosecond – sub picoseconds electron bunch is peaked in the millimeter wave and THz spectrum range. Moreover the emission intensity increases inversely with the bunch length. Hence measuring intensity changes provides an estimation of the relative bunch length variation, that is extremely useful but does not give the actual bunch length in absolute terms. To perform an absolute bunch length measurement several ingredients are needed. The first one consists in finding an analytical formalism able to describe the physics of the system. In our device we detect the coherent diffracted radiation emitted by the electron bunch passing a ceramic gap. Despite this system has a formal analytical solution of its corresponding Maxwell problem, the latter is very complex and hardly usable for practical applications. For this reason we have found an analytical approximation that can be used to calculate the bunch length from our device. This is the first ingredient. Then, the intensity depends on the Fourier transform of the longitudinal current distribution.
of the bunch (i.e. its shape). The Fourier transform contains much more information than needed, since we wanted only a robust measure of the bunch length. But if we choose the detection frequency properly low and with a relatively small bandwidth we can measure only the bunch length dependence without being effected by the bunch shape details. This is the second ingredient.

The third ingredient is a proper feature of the coherent emission from a gap in a waveguide. As the bunch gets shorter the emitted signal intensity increases but its derivative tends to zero for very short bunches. This behavior is asymptotic and it is indeed the key property of the proposed method. Now putting all ingredients together we can use the approximation for the theory and a general dependence on the bunch length. Experimentally, the self-calibration method consists in varying the bunch length while detecting the diffraction signal until reaching the asymptotic value. We fit the obtained curve with the theory, where we demonstrated that the only free parameter is a scaling factor. At this point the system device is calibrated and available to provide absolute bunch length measurements.

We validate the described method on the FERMI linac, by changing the longitudinal compression factor (i.e the L01 rf phase) in the first magnetic chicane (BC1) and detecting the coherent signal from the gap by means of a 30 GHz Schottky diode for 200 pC and 350 pC bunches installed in the Coherent Bunch Length Monitor (CBLM). The results are reported in Fig. 1. Bunch lengths as measured by CBLM (red dots) are compared with bunch lengths measured with the RF deflecting cavity (blue curve). Figure shows a very good agreement and proves the independence of the proposed method from the bunch charge. The results can be applied to different accelerators providing a shot by shot, nondestructive, absolute bunch length measurement with unprecedented simplicity.

![Graph showing bunch length measurement validation CBLM (red) vs deflecting cavity (blue).](image)

Figure 1. Bunch length measurement validation CBLM (red) vs deflecting cavity (blue). Reprinted with permission from DOI:10.1103/PhysRevLett.110.074802.

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**Original Paper**


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The energy spectrometer and the focusing systems installed along the photon beam transport of FERMI have been extensively used during the commissioning and the external users’ experiments. The PRESTO (Pulse Resolved Energy Spectrometer, Transparent and Online) has been operated both to monitor the performance of the FEL emission and to characterize it in special conditions (as requested by the users). The KAOS (Kirkpatrick-Baez Active Optics Systems) have been employed to create controllable-size photon beam spots on the samples, reaching almost the smallest possible sizes when needed.

After the successful commissioning of FEL-1, FERMI has been opened to external users in December 2012. The first experiments were carried out in the three operative endstations: DiProI, LDM, and EIS-TIMEX. The PADReS (Photon Analysis, Delivery and Reduction System), after the intensive use during the FERMI commissioning, has been routinely and profitably used during the experiments to determine photon beam pulse characteristics like the intensity, the spectral purity, the emission mode, etc., as well as to transport and manipulate the radiation.

The system is installed after the undulator chains, extending down to the endstations, and it is composed by sections dedicated to different measurements as well as by elements intended to control the intensity and the focusing of the photon beam. All of them, except for the insertable screens, work in a non-invasive and shot-to-shot fashion, characterizing each single FEL pulse delivered to the experiments.

PRESTO is the energy spectrometer installed at the beginning of the experimental hall, on an optical path common to all the three beamlines. It works sending ~97% the unperturbed FEL radiation to the endstations, while diffracting and focusing part of it (~1-2%) in order to determine the spectrum of each single pulse (Fig. 1a). To accomplish this task it is endowed by two diffraction gratings (selectable depending on the wavelength in use) that are plane in shape. In this way, used in specular reflection (“0 order”), the gratings behave as mirrors, not modifying the geometrical characteristics of the FEL beam (angular divergence, wavefront, and so on) sent to the following transport system. The diffracted part, on the other way, is focused in the horizontal direction by the gratings’ variable line spacing groove density onto a YAG screen imaged by a CCD camera. In this way, by measuring the shape of the image acquired by the CCD it is possible to reconstruct the spectrum, obtaining, for each shot, the central wavelength, the BW.

![Figure 1. a) single shot image as acquired by the CCD camera. Integrating in the vertical direction the spectrum is obtained; b) single shot spectra of the 2-color double pulse; c) intensities of the individual pulses as inferred from the spectra in b).](image-url)
With PRESTO it has then been possible to characterize the FEL emission also in terms of stability of both the central wavelengths and the BW.

Due to the high resolution of PRESTO (Resolving power ≥ 15000 in the whole 100-2.3nm range) it has been possible also to easily discriminate between the two ~500fs-delayed FEL pulses used during 2-color pump-probe experiments (2 colors: ∆λ=0.2nm; PRESTO resolution: 0.002nm – Fig.1b). Moreover, it has been employed to determine the intensities of the two pulses, which were too close in time to be distinguished by the gas-based intensity monitors routinely used at FERMI (Fig.1c). This information has been obtained by integrating the area below each of the two pulses, as acquired on the PRESTO CCD.

In this way several advantages are obtained: the optical surface quality of the mirrors can be quite high (as plane surfaces are easier to be manufactured and finished), the horizontal and vertical focusing are decoupled, and the focusing can be adapted to the different FEL (1 or 2) in use. The bending is realized by mechanical actuators that deforms the mirror holder, transmitting the deformation to the 10mm-thick (400mm-long and 40mm-wide) fused silica mirror. The working deformation in the center of the mirror, with respect to the plane shape, is about 200µm in height.

KAOS has been successfully used during both tests and experiments, providing an adjustable focusing capable of creating a small focal spot on the sample in the standard endstation as well as in additional endstations installed after it. Spot dimensions as small as ~10µm in diameter have been obtained upon proper optimization by means of visible screens as well as wavefront sensing (Fig. 2b). The results have been confirmed also by post-mortem analysis of single-shot-damaged samples (Fig. 2c-d).

Figure 2. a) mechanical bender of one of the KAOS mirrors; b) FEL spot transverse distribution reconstructed from wavefront sensor analysis; c) single shot indentation on PMMA sample; d) single shot damage of a Si sample.

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Two different seeding schemes, recently developed at the FERMI@Elettra free electron laser, allow generation of two-color FEL pulses with precisely controlled wavelength, intensity and timing, making the source an ideal playground for FEL based pump-probe experiments. The potential of such schemes to explore transient states of matter with elemental sensitivity is demonstrated by diffraction experiments with Ti grating, tuning the two pulses to the Ti M-resonance and varying their intensity.

Understanding the exotic properties of matter driven to extreme non-equilibrium states by interaction with very intense VUV/x rays, has become possible with the advent of ultrabright free electron lasers (FEL). Development of different photon correlation schemes, with temporal and spatial resolution determined only by the FEL pulse duration and wavelength, are key steps towards accessing ultra-fast dynamic phenomena. The dynamics is initiated by the first “pump” pulse, which generates carriers at time scales shorter than carrier diffusion and electron-phonon scattering. The evolution of the transient states is then monitored by a second “probe” pulse arriving at variable and defined time delay. Tuning the pulse wavelengths to atomic resonances opens an unprecedented opportunity to add selectively elemental sensitivity to the measurement, which is essential for exploring ultrafast processes in morphologically complex multicomponent materials.

Addressing the growing interest in using multi-color FEL pulses for ultrafast science the scientists at Elettra-Sincrotrone Trieste demonstrated the possibility of operating FERMI FEL in regimes suited to perform two-color pump-probe experiments in the XUV or x ray domain.

In the standard single pulse operation mode the electron bunch of FERMI-FEL is seeded with a single laser pulse with peak intensity tuned to maximize the emission from the central part of the electron beam. The adopted seed-scheme of FERMI-FEL has allowed generation of two-color pulses, using the methods illustrated in Fig. 1 a and b. The first two-color FEL scheme (Fig. 1 a) exploits the FEL saturation dynamics to split the pulse in two parts by seeding the electron bunch with a powerful laser pulse, carrying a significant frequency chirp. At seeding peak intensities above a given power threshold, the pulse degrades the micro-bunching in the central part of the electron beam, emitting only from the tails, separated in time, generating two temporal and spatially separated pulses.

Figure 1. (a) Generation of two-color pulses using powerful seed laser pulse which carries significant frequency chirp. The right panel shows the wavelength split as a function of seed power. (b) Generation of two-color pulses using two independent seed laser pulses with slightly different central wavelengths. The right panel shows sequence of consecutive two-color spectra where the green dash lines highlight the intentional suppression of one of the FEL pulses.
of the seeded area. The spectrum of the splitted FEL pulses shows that these have a wavelength difference of 0.2 nm, with a time separation in the range 90-160 fs. We expect to reach 50 - 30 fs in the future.

The second two-color FEL scheme, illustrated in Fig. 1 b, uses two independent seed laser pulses with slightly different central wavelengths, $$\lambda_{1,\text{seed}}$$ and $$\lambda_{2,\text{seed}}$$, with variable time separation and intensity ratio. The two electron bunch seeded regions emit two independent, temporally separated FEL pulses at the harmonics of the seed wavelengths $$\lambda_1 = \lambda_{1,\text{seed}} / N$$ and $$\lambda_2 = \lambda_{2,\text{seed}} / N$$ respectively. The time separation between these two-color pulses can be controlled by tuning the delay between the input seed pulses. By blocking one of the seed laser arms one can easily switch between single and double FEL emission. The time separation depends on the laser pulse length and on the effective electron bunch extension. Presently the time separation can be varied in the range 150 fs – 800 fs and can be extended beyond 1 ps in the future.

The potential of the second twin-pulse seed scheme to explore transient states of matter, stimulating and probing electronic transitions from core levels is demonstrated by a pilot pump-probe experiment with Ti grating structure deposited on a Si$_3$N$_4$ window, sketched in Fig. 2. The selected wavelengths of both the pump ($$\lambda_1 = 37.2$$ nm) and probe ($$\lambda_2 = 37.4$$ nm) pulses are within the slope region of the Ti M$_{23}$ absorption resonance, where the Bragg peak intensities and positions are very sensitive to the instantaneous Ti ionization state. The results displayed in Fig. 2 show that at low ‘pump’ and ‘probe’ intensities, the diffraction pattern is a simple sum of the ‘pump’ and ‘probe’ Bragg peaks. Using a very intense ‘pump’ pulse, the diffraction pattern undergoes an abrupt change due to dramatic loss of the ‘probe’ Bragg peak intensity. Since the sum of the delay time (≈500 fs) and pulse duration (≈100 fs) is shorter than those of hydrodynamic expansion and ablation, this result can be explained only by dramatic changes in the Ti electronic structure, namely highly ionized states of Ti atoms that pushes the M- resonance to shorter wavelengths.

This pilot experiment shows that multi-color studies with element specificity, can be carried out with sub ps time resolution, essential for addressing many gaps in our knowledge for interactions between atomic constituents or spatially separate phases or units in matter.

**Original Papers**


E. Allaria et al., Nat. Commun. 4:2476 (2013); DOI:10.1038/ncomms3476.

**Figure 2.** (Left) Two-color FEL pulses, $$\lambda_1$$ and $$\lambda_2$$, tuned across the Ti M-resonance, impinge on a Ti grating with a temporal separation, $$\Delta t$$. (Right) Diffraction patterns corresponding to single color ‘pump’ and ‘probe’ pulses and to two-color ‘pump’-‘probe’ pulses (delayed by 500 fs) for different flux ($$F$$) regimes: low-$$F = 10^{-30} \text{ mJ/cm}^2$$, high-$$F = 2 \text{ J/cm}^2$$. 

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**E. Allaria$^1$, F. Bencivenga$^1$, R. Borghes$^1$, F. Capotondi$^1$, D. Castronovo$^1$, P. Charalambous$^2$, P. Cinquegrana$^1$, M. B. Danailov$^1$, G. De Ninno$^{1,3}$, A. Demidovich$^1$, S. Di Mitri$^1$, B. Diviacco$^1$, D. Fausti$^{1,4}$, W. M. Fawley$^1$, E. Ferrari$^1$, L. Froehlich$^1$, D. Gauthier$^1$, A. Gessini$^1$, L. Giannessi$^{1,5}$, R. Ivanov$^1$, M. Kiskinova$^1$, G. Kurdi$^1$, B. Mahieu$^{1,6}$, N. Mahne$^1$, I. Nikolov$^1$, C. Masciovecchio$^1$, E. Pedersoli$^1$, G. Penco$^1$, L. Raimondi$^1$, C. Serpico$^1$, P. Sigalotti$^1$, S. Spampinati$^1$, C. Spezzani$^1$, M. Trovò$^1$ and M. Zangrando$^{1,8}$

$^1$ Sincrotrone Trieste S.c.p.A., Trieste, Italy.

$^2$ Zone Plates Ltd, London, UK.

$^3$ Laboratory of Quantum Optics, University of Nova Gorica, Nova Gorica, Slovenia.

$^4$ Department of Physics, University of Trieste, Trieste, Italy.

$^5$ ENEA CR Frascati, Rome, Italy.

$^6$ Service des Photons Atomes et Molécules, CEA, Saclay, France.

$^7$ IOM-CNR, Laboratorio TASC, Trieste, Italy.

e-mail: luca.giannessi@elettra.eu, giovanni.dennino@elettra.eu, maya.kiskinova@elettra.eu
Facts & Figures
Events
**Elettra Sincrotrone Trieste** is an international research centre specialized in the study of materials through a highly versatile and powerful tool: synchrotron light.

The centre hosts two different synchrotron light sources: Elettra, a third-generation storage ring after which the centre itself is named, and FERMI, a cutting-edge free electron laser, together with a number of support laboratories.

The centre plays a leading role in the development of joint projects between European research facilities: Elettra is the coordinator of the networks promoting transnational access to synchrotrons and free electron lasers, the development of shared activities, and the strengthening of services provided to clients. Elettra is also an associate of IAEA, the International Atomic Energy Agency (established in 1957 within the framework of the United Nations for the peaceful use of nuclear technology) and is part of the primary science and technology network of the Central European Initiative (CEI).

On its site Elettra hosts the National Tasc Laboratory (IOM-CNR), a facility for micromanufacturing and nanoscience. It has also established enduring working relationships with important Italian and foreign institutions, including various Italian National Research Council institutes, the Academy of Science of the Czech Republic, UNESCO’s International Centre for Theoretical Physics (ICTP), the Indian Institute of Science, the International School of Advanced Studies (ISAS/SISSA) and the Universities of Graz, Milan, Nova Gorica, Trento, Trieste and Udine. These partners are actively contributing to the construction and operation of beamlines and support laboratories. Elettra’s scientific and technical quality and developments are constantly monitored by board-appointed international Committees, which advise on all relevant aspects of the general and development policy, scientific programs, accelerator development, technology transfer and industrial applications.

### ALLIANCES AND PARTNERSHIPS
- Academy of Sciences of the Czech Republic
- CEI (Central European Initiative)
- Charles University in Prague
- CNR (Italian National Research Council)
- CNRS (French National Research Council)
- Institut für Festkörperforschung Forschungszentrum Jülich
- ICTP - UNESCO (International Centre for Theoretical Physics)
- IAEA (International Atomic Energy Agency)
- Indian Institute of Science, Bangalore
- INFN (Institute of Nuclear Physics)
- INSTM (National Inter-University Consortium for Materials Science and Technology)
- IRUVX (European Consortium for FELs up to the UV/softXray)
- ISAS/SISSA (International School of Advanced Studies)
- TU GRAZ (Graz University of Technology)
- University of Milan – Bicocca
- University of Nova Gorica
- University of Trento
- University of Trieste
- University of Udine

### SHAREHOLDERS
The centre is managed by Elettra – Sincrotrone Trieste S.C.p.A., a non-profit Share Company (Società Consortile per Azioni) of national interest pursuant to Law 370/99. The shareholders are:

- AREA Science Park Consortium (53.7%),
- Autonomous Region of Friuli Venezia Giulia (37.63%)
- CNR (Italian National Research Council) (4.85%)
- Invitalia Partecipazioni S.p.A. (3.82%)
Elettra Sincrotrone Trieste is managed by a **Board of Directors**, assisted by a shareholder-appointed **Board of Auditors**, and advised by board-appointed international committees such as the **Council of Partners** for general and development policy, the **Scientific Advisory Council** for scientific programs and the **Machine Advisory Committee** for accelerator development.

**Board of Directors**
- **President**: Carlo Rizzuto
- **Vice President**: Giovanni Comelli
- **Chief Executive Officer**: Alfonso Franciosi
- Marcello Fontanesi
- Gemma Luisa Ravizza

**Board of Auditors**
- **President**: Cristina Aimici
- Paolo Marchesi
- Marco Posocco

**Council of Partners**
- **President**: Carlo Rizzuto
- Fabio Barbone
- Stefano Fantoni
- Alain Fontaine
- Marcello Fontanesi
- Dante Gatteschi
- Peter Laggner
- Vladimir Matolin
- Claudio Tuniz

**MAC**
- **Machine Advisory Committee**
  - **Chairman**: Richard P. Walker
  - Hans Braun
  - Paul Emma
  - Mikael Eriksson
  - Peter Kuske
  - Amor Nadji
  - Claudio Pellegrini
  - Ferdinand Willeke
  - Sasha Zholents

**SAC**
- **Scientific Advisory Council**
  - **Chairman**: Ingolf Lindau
  - Karsten Horn
  - Sine Larsen
  - Keith Nelson
  - Bruce Patterson
  - Maria Novella Piancastelli
  - Jean-Pierre Samama
  - Charles V. Shank
  - Robert W. Schoenlein
  - Wilfried Wurth

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**Diagram:**
- **Board of Directors**
  - **President**
  - **Vice President**
  - **Chief Executive Officer**
- **Board of Auditors**
- **Council of Partners**
- **MAC**
- **SAC**
- **Strategic Committee**
- **Executive Committee**
- **Project Clusters & Groups**
## Beamlines

### Elettra Beamlines

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<tr>
<th>Source</th>
<th>Energy Range (eV)</th>
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<td><strong>1.1L</strong> TWINMIC</td>
<td>High resolution soft x ray transmission and emission twin microscope short id</td>
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<tr>
<td><strong>1.2L</strong> Nanospectroscopy</td>
<td>X ray photoemission electron microscopy (XPEEM) and microprobe ARPES</td>
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<tr>
<td><strong>1.2L</strong> NanoESCA</td>
<td>Imaging XPEEM spectroscopy, microprobe ARPES and XPS</td>
</tr>
<tr>
<td><strong>1.2R</strong> Storage ring FEL</td>
<td>European Free-Electron Laser Project</td>
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<tr>
<td><strong>2.2L</strong> ESCA Microscopy</td>
<td>Scanning photoelectron microscopy (SPEM)</td>
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<tr>
<td><strong>2.2R</strong> SuperESCA</td>
<td>Fast and high energy resolution photoemission and absorption spectroscopy</td>
</tr>
<tr>
<td><strong>3.2L</strong> Spectro Microscopy</td>
<td>Angle-resolved photoemission microscope</td>
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<tr>
<td><strong>3.2R</strong> VUV Photoemission</td>
<td>Angle-resolved photoelectron spectroscopy (ARPES) in the VUV range</td>
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<tr>
<td><strong>4.2</strong> Circular Polarization</td>
<td>Dichroic measurements on chiral systems</td>
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<td><strong>5.2L</strong> SAXS</td>
<td>Small Angle X ray Scattering</td>
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<tr>
<td><strong>5.2R</strong> XRD1</td>
<td>X Ray Diffraction</td>
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<tr>
<td><strong>6.1L</strong> Materials science</td>
<td>Photoemission and x ray absorption</td>
</tr>
<tr>
<td><strong>6.1R</strong> SYRMEP</td>
<td>Synchrotron Radiation for Medical Physics</td>
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<td><strong>6.2R</strong> Gas Phase</td>
<td>Spectroscopy of atoms, molecules and clusters in the VUV and soft x rays</td>
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<td><strong>7.1</strong> MCX</td>
<td>Powder diffraction beamline</td>
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<td><strong>7.2</strong> ALOISA</td>
<td>Advanced Line for Overlayer, Interface and Surface Analysis</td>
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<td><strong>8.1L</strong> BEAR</td>
<td>Bending magnet for Emission Absorption and Reflectivity</td>
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<td><strong>8.2</strong> BACH</td>
<td>Beamline for Advanced Dichroism</td>
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<td><strong>9.1</strong> SISSI</td>
<td>Synchrotron Infrared Source for Spectroscopy and Imaging</td>
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<td><strong>9.2</strong> APE</td>
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<td><strong>11.2C</strong> XRD2</td>
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<td><strong>11.2L</strong> XPRESS</td>
<td>X ray Diffraction High Pressure Experiments</td>
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**Source**

- *id = insertion device (wiggler or undulator)*
- *bm = bending magnet*

### FERMI Beamlines

<table>
<thead>
<tr>
<th>Source</th>
<th>Wavelength Range</th>
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<td><strong>TeraFERMI</strong></td>
<td>TeraHertz beamline at FERMI</td>
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<td><strong>MagneDyn</strong></td>
<td>Magneto Dynamics Studies</td>
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<tr>
<td><strong>LDM</strong></td>
<td>Low Density Matter: atomic, molecular, and optical science with rarefied targets</td>
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<tr>
<td><strong>DiProl</strong></td>
<td>Diffraction and Projection Imaging</td>
</tr>
<tr>
<td><strong>EIS-TIMEX</strong></td>
<td>Elastic and Inelastic Scattering: Ultrafast Time-resolved studies of Matter under Extreme and metastable conditions</td>
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<tr>
<td><strong>EIS-TIMER</strong></td>
<td>Elastic and Inelastic Scattering: TIME-Resolved spectroscopy of nanoscale dynamics in condensed matter physics</td>
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</table>
Access to **Elettra** and **FERMI** beamlines is offered every year to scientists from more than 50 different countries based on the scientific merit of the proposals they submit. The most deserving proposals are selected by independent Proposal Review Panels of world-renowned experts in synchrotron radiation research and applications, appointed by the laboratory management.

The Elettra and FERMI Panels are divided into subpanels, each of them reflecting different research areas. These panels meet twice a year, producing a written report for each proposal. Best ranked proposals are allocated according to the amount of available user dedicated beamtime.

### Elettra Proposal Review Panel

<table>
<thead>
<tr>
<th>Panel</th>
<th>Chairman</th>
<th>Members</th>
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<tbody>
<tr>
<td>A - Atoms Molecules and Plasmas</td>
<td>Carlo MARIANI</td>
<td>Vincenzo AQUALANTI, Uwe Yu Eugen BECKER, John Malcolm DYKE</td>
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<td>C - Catalytic Materials/Surface Science</td>
<td>Carlo MARIANI</td>
<td>Maria Carmen ASENSIO, Karol HRICOVIN, Adam Fraser LEE, Falko NETZER, Luca OTTAVIANO, Michele Rose SAUVAGE SIMKIN</td>
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<tr>
<td>H - Condensed matter - Electronic and Magnetic Structure</td>
<td>Maurizio SACCHI</td>
<td>Alexei V. FEDOROV, Mark GOLDEN, Wolfgang KUCH, Giorgio MARGARITONDO, Marino MARSI, Enrique GARCIA MICHEL, Danilo PESCIA, Jan VOGEL</td>
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<tr>
<td>ILP - Instrumentation and Technological materials - Life and Medical Sciences (excluding Crystallography) - Polymers and Soft Matter</td>
<td>Graeme R. MORRISON</td>
<td>Alberto BRAVIN, Gianfelice CINQUE, Paul DUMAS, Christopher John HALL, Enzo LOMBI, Lisa MILLER, Gunter SCHMAHL, Andrew Duncan SMITH, Mark TOBIN</td>
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<tr>
<td>M - Protein and Macromolecular Crystallography</td>
<td>Giuseppe ZANOTTI</td>
<td>Peter BRICK, Dusan TURK, Luigi VITAGLIANO</td>
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<td>S - Hard condensed matter - Structures</td>
<td>Maurizio BENFATTO</td>
<td>Robert Joseph CERNIK, Giuseppe CRUCIANI, Paola D’ANGELO, Marco MILANESIO, Fred MOSSELMANS, Maria Grazia PROIETTI</td>
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<td>T - Scattering</td>
<td>Paolo MARIANI</td>
<td>Stephanie Brigitte FINET, Daniele FIORETTO, Hermann FRANZ, Giulio MONACO</td>
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### FERMI Proposal Review Panel

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<tr>
<td>Janos KIRZ</td>
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<tr>
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Users at Elettra

II semester 2012 - I semester 2013
Proposals submitted: 773
Proposals allocated: 424

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<td><strong>Others</strong></td>
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<td><strong>1076</strong></td>
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* Croatia is a member of the EU from 1 July 2013
Users at FERMI

December 2012 - March 2013
Proposals submitted: 32
Proposals allocated: 14

October 2013 - July 2014
Proposals submitted: 45
Proposals allocated: 20
Elettra Sincrotrone Trieste has adopted a matrix-type of organization. There are five Strategic Initiatives, which correspond to distinct Project Clusters: Elettra, FERMI, Research, Technology Platform and International Project, grouped together based on the complementarity of the different project goals. The human and instrumental resources required by the different projects are managed within nine Groups of staff members with similar or related expertise.

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<thead>
<tr>
<th>CLUSTERS</th>
<th>Scientists and Researchers</th>
<th>Technical Personnel</th>
<th>Administrative and clerical Personnel</th>
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<td></td>
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<td>34</td>
</tr>
<tr>
<td>General Services*</td>
<td></td>
<td></td>
<td></td>
<td>60</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td></td>
<td></td>
<td></td>
<td><strong>365</strong></td>
</tr>
</tbody>
</table>
## Budget allocation for 2013

### Running costs

<table>
<thead>
<tr>
<th>Category</th>
<th>2013</th>
</tr>
</thead>
<tbody>
<tr>
<td>General costs</td>
<td>9,176,301</td>
</tr>
<tr>
<td>Personnel</td>
<td>11,500,000</td>
</tr>
<tr>
<td>Utilities</td>
<td>5,029,162</td>
</tr>
<tr>
<td>Accelerator Group</td>
<td>109,599</td>
</tr>
<tr>
<td>Administration Group</td>
<td>218,915</td>
</tr>
<tr>
<td>Beamlines Group</td>
<td>950,656</td>
</tr>
<tr>
<td>General services Group</td>
<td>1,018,309</td>
</tr>
<tr>
<td>Electromagnetism Group</td>
<td>161,968</td>
</tr>
<tr>
<td>IT Group</td>
<td>244,458</td>
</tr>
<tr>
<td>Infrastructure Group</td>
<td>876,542</td>
</tr>
<tr>
<td>Mechanical, Vacuum and Optical Engineering Group</td>
<td>277,289</td>
</tr>
<tr>
<td>Industrial Liaison Office operation</td>
<td>650,000</td>
</tr>
<tr>
<td>Scientific partnerships</td>
<td>1,020,577</td>
</tr>
<tr>
<td>OPAC</td>
<td>1,168,643</td>
</tr>
<tr>
<td>Development projects</td>
<td>961,770</td>
</tr>
<tr>
<td><strong>Total Ordinary operation</strong></td>
<td><strong>33,364,189</strong></td>
</tr>
</tbody>
</table>

### Special projects

<table>
<thead>
<tr>
<th>Category</th>
<th>2013</th>
</tr>
</thead>
<tbody>
<tr>
<td>FERMI</td>
<td>22,930,625</td>
</tr>
<tr>
<td>International Infrastructure projects</td>
<td>16,850,000</td>
</tr>
<tr>
<td><strong>Total special projects</strong></td>
<td><strong>39,780,625</strong></td>
</tr>
</tbody>
</table>

**GENERAL TOTAL** 73,144,814
2012 was extremely successful in attracting resources from external funding institutions: the funds acquired through research contracts amount to about 3.8 million Euro. A substantial decrease will result in 2013 as consequence of the end of the 2007-2013 funding round: the funds acquired through research contracts in the first nine months of 2013 amount to about 0.9 million Euro.

In this reporting period, Elettra participated in 44 research contracts (see table) funded by the following external agencies: European Commission, European Science Foundation, Italian Ministry of Research, Italian Ministry of Economic Development, Italian Ministry of Foreign Affairs, Region Friuli-Venezia Giulia, Italian Association for Cancer Research, International Centre for Theoretical Physics, Indian Department of Science and Technology.

The leadership of Elettra among the European Research Infrastructures is highlighted by its role of Coordinator of the CALIPSO and RAMIRI 2 projects.

At the time of this writing, CALIPSO (www.calipso.wayforlight.eu) is running towards its first milestones: standardized datasheets for all European beamlines are ready to be published on the unified web portal www.wayforlight.eu. In the next months, wayforlight will offer a single-sign-on service (www.umbrellaid.org) allowing login to all European synchrotrons web-based unified offices and access to interactive search tools to find the best beamline for each experiment.

The RAMIRI 2 project developed a Handbook (www.ramiri-blog.eu) which is intended as an introductory instrument for people who need a quick access to the main definitions and references on the major issues related to Research Infrastructures, aiming at developing a common understanding and cultural basis between RIs managers, users and policy makers at the various levels.

Building on this good reputation in research management related issues, Elettra is further enhancing its guidance role within the European Research Infrastructures landscape by the development of the Central European Research Infrastructure Consortium (CERIC-ERIC: see www.ceric-eric.eu). After an in-depth and fruitful discussion with the European Commission, CERIC-ERIC is now in the final phase of approval, which is expected in the next few months.
## Running research contracts

### European/International Research Contracts

<table>
<thead>
<tr>
<th>NAME</th>
<th>SHORT NAME</th>
<th>COORDINATOR</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICTP-Elettra Users Programme</td>
<td></td>
<td>Elettra – Sincrotrone Trieste SCpA</td>
</tr>
<tr>
<td>Transnational access of the Indian scientists to the Elettra beamlines</td>
<td></td>
<td>Elettra – Sincrotrone Trieste SCpA</td>
</tr>
<tr>
<td>Coordinated Access to Lightsources to Promote Standards and Optimization</td>
<td>CALIPSO</td>
<td>Elettra – Sincrotrone Trieste SCpA</td>
</tr>
<tr>
<td>Transnational access and enhancement of integrated Biological Structure determination at synchrotron X-ray facilities</td>
<td>BioStruc-X</td>
<td>EMBL, Germany</td>
</tr>
<tr>
<td>Realising and Managing International Research Infrastructures 2</td>
<td>RAMIRI 2</td>
<td>Elettra – Sincrotrone Trieste SCpA</td>
</tr>
<tr>
<td>TIME-Resolved Spectroscopy of Nanoscale Dynamics in Condensed Matter Physics</td>
<td>Timer</td>
<td>Elettra – Sincrotrone Trieste SCpA</td>
</tr>
<tr>
<td>Advanced European lithium sulphur cells for automotive applications</td>
<td>EUROLIS</td>
<td>National Institute of Chemistry, Slovenia</td>
</tr>
<tr>
<td>Phase Change Memory Advanced universal Switches through Thin alterRnting laYers</td>
<td>PASTRY</td>
<td>Micron Semiconductor Italia Srl, Italy</td>
</tr>
<tr>
<td>Governing ultrafast the conductivity of correlated materials</td>
<td>GO FAST</td>
<td>SISSA, Italy</td>
</tr>
<tr>
<td>Photon and Neutron Data - Open Data Infrastructure</td>
<td>PanDataODI</td>
<td>STFC, United Kingdom</td>
</tr>
<tr>
<td>Maximizing Synergies for Central European Biotech Research Infrastructures</td>
<td>SynBioOsis</td>
<td>JC zipro, Czech Republic</td>
</tr>
<tr>
<td>CEI Research Fellowship Programme</td>
<td>CERES</td>
<td>INCE - Central European Initiative, Italy</td>
</tr>
<tr>
<td>Central European Network for knowledge based on Innovative Light Sources</td>
<td>CENILS</td>
<td>Elettra – Sincrotrone Trieste SCpA</td>
</tr>
<tr>
<td>Executive programme of scientific and technological co-operation between the Italian Republic and Republic of South Africa for the year 2011-2013</td>
<td>SISTER-MAE</td>
<td>Elettra – Sincrotrone Trieste SCpA</td>
</tr>
<tr>
<td>Synchrotron X-ray µ-Tomography with rare earth based nanoparticles as contrast agents for enhanced biomedical imaging; MicroCT with nanoparticle-based contrast agents for biomedical imaging - Joint project: Italy-Sweden</td>
<td>NP-based-MicroCT</td>
<td>Elettra – Sincrotrone Trieste SCpA</td>
</tr>
<tr>
<td>Understanding and Manipulating Enzymatic and Proteomic Processes in Bimineralization</td>
<td>COST ACTION TD0903</td>
<td>Elettra – Sincrotrone Trieste SCpA</td>
</tr>
<tr>
<td>Researchers’ Night</td>
<td>NEAR 2013</td>
<td>University of Trieste, Italy</td>
</tr>
</tbody>
</table>

### National Research Contracts

<table>
<thead>
<tr>
<th>NAME</th>
<th>SHORT NAME</th>
<th>COORDINATOR</th>
</tr>
</thead>
<tbody>
<tr>
<td>FERMIL@Elettra - Phase II</td>
<td>FERMIL@Elettra - Phase II</td>
<td>Elettra – Sincrotrone Trieste SCpA</td>
</tr>
<tr>
<td>Elucidation of the structure and function of MCM Helicases</td>
<td>AIRC-MCM</td>
<td>Elettra – Sincrotrone Trieste SCpA</td>
</tr>
<tr>
<td>Analysis of the human RECQ1 helicase function in DNA replication and repair</td>
<td>AIRC-RECQ1</td>
<td>Elettra – Sincrotrone Trieste SCpA</td>
</tr>
<tr>
<td>Application of Advanced Nanotechnology in the Development of Innovative Cancer Diagnostics Tools</td>
<td>AIRC-Nanodiagnostics</td>
<td>CRO Aviano - National Cancer Institute, Italy</td>
</tr>
<tr>
<td>“Production, management and distribution systems for photovoltaic electric power”</td>
<td>ERG</td>
<td>STMicroelectronics Srl, Italy</td>
</tr>
<tr>
<td>Photocatalytic nanosystems for artificial photosynthesis and hydrogen production by solar-driven water splitting</td>
<td>NANOSOLAR</td>
<td>University of Messina, Italy</td>
</tr>
<tr>
<td>Development and production of high performance biocompatible and multifunctional innovative materials</td>
<td>PROCERPOL</td>
<td>Lima Lto. SpA, Italy</td>
</tr>
</tbody>
</table>

### Regional/Cross Border Research Contracts

<table>
<thead>
<tr>
<th>NAME</th>
<th>SHORT NAME</th>
<th>COORDINATOR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Realization of a technological platform for the crystallographic analysis of biological macromolecules of biomedical interest for the industrial research</td>
<td>DAGEAS</td>
<td>Elettra – Sincrotrone Trieste SCpA</td>
</tr>
<tr>
<td>Development and realization of solid state ultrafast laser amplifiers optimized for FEL applications</td>
<td>FEMTOREG</td>
<td>Elettra – Sincrotrone Trieste SCpA</td>
</tr>
<tr>
<td>Development of chemical sensors for environmental and biological diagnosis based on nanowires and nanotubes</td>
<td>AMBIOSEN</td>
<td>Elettra – Sincrotrone Trieste SCpA</td>
</tr>
<tr>
<td>Studies on the decay mechanisms of nanomaterials and their potential dangers in biological systems</td>
<td>NANOTOX</td>
<td>Elettra – Sincrotrone Trieste SCpA</td>
</tr>
<tr>
<td>Studies and characterization of high power X-band (12 GHz) radiofrequency devices</td>
<td>X-BAND</td>
<td>Elettra – Sincrotrone Trieste SCpA</td>
</tr>
<tr>
<td>Study of a femtosecond timing system for new synchrotron light sources</td>
<td>SYRATIM@FS</td>
<td>Elettra – Sincrotrone Trieste SCpA</td>
</tr>
<tr>
<td>Dynamics of macromolecular and biological systems via Raman spectroscopy with ultrashort pulses</td>
<td>MASPERA</td>
<td>Elettra – Sincrotrone Trieste SCpA</td>
</tr>
<tr>
<td>Study for a photoinjector capable of supplying a 50Hz pulsed beam with very high brilliance</td>
<td>HIBEGuS</td>
<td>Elettra – Sincrotrone Trieste SCpA</td>
</tr>
<tr>
<td>Imaging - Service Oriented Infrastructure</td>
<td>I-SO1</td>
<td>Elettra – Sincrotrone Trieste SCpA</td>
</tr>
<tr>
<td>Interregional Centre of Ultrafast Photonic Technologies for Spectroscopy</td>
<td>CITIUS</td>
<td>University of Nova Gorica, Slovenia</td>
</tr>
<tr>
<td>Identification of new cancer stem cell markers for diagnostic and therapeutic purposes</td>
<td>GLOIMA</td>
<td>National Institute of Biology, Slovenia</td>
</tr>
<tr>
<td>The cross-border proteins centre for cancer diagnostic and research</td>
<td>PROTEO</td>
<td>Elettra – Sincrotrone Trieste SCpA</td>
</tr>
<tr>
<td>Set-up and test of models for optimized use of photovoltaic energy</td>
<td>MODEF</td>
<td>Elettra – Sincrotrone Trieste SCpA</td>
</tr>
<tr>
<td>Experimentation of an extra-fine thermostating system for particle accelerators</td>
<td>TEXA</td>
<td>Elettra – Sincrotrone Trieste SCpA</td>
</tr>
<tr>
<td>Free-electron-laser based analysis of nanostructures in supersonic beams</td>
<td>ANGEL</td>
<td>Elettra – Sincrotrone Trieste SCpA</td>
</tr>
<tr>
<td>User-friendly domotic systems based on smart lighting devices</td>
<td>EASYHOME</td>
<td>Centro Ricerche Plast-Optica SpA, Italy</td>
</tr>
</tbody>
</table>

### Instrn-Mediated Research Contracts

<table>
<thead>
<tr>
<th>NAME</th>
<th>SHORT NAME</th>
<th>COORDINATOR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanotechnological approaches toward tumor theragnostic</td>
<td></td>
<td>University of Trieste, Italy</td>
</tr>
<tr>
<td>TerraFermi - A THz beamline at the FERMI Free Electron Laser</td>
<td></td>
<td>INSTM, Italy</td>
</tr>
<tr>
<td>SUPRAmoleculary Templated Synthesis of Homochiral CARBON Nanotubes for Photovoltaic Applications</td>
<td></td>
<td>University of Trieste, Italy</td>
</tr>
</tbody>
</table>
Industrial Liaison Office

The Industrial Liaison Office (ILO) was set-up in 2004 to promote the exceptional body of skills and technical expertise resulting from the experience accumulated in the construction and operations of the Elettra facilities. The Industrial Liaison Office supplies advanced instrumentation to other Synchrotron Facilities and Research Laboratories and provides products and services to private companies operating in different fields: mechanics, optics, pharmaceutica, microelectronics, energy, chemistry, agri-foodstuffs etc.

Collaboration with Industry mainly concerns:
- Analytical and metrological services on the micro-nanoscale for characterization of the chemical-physical and electronic structure of materials and devices: industry pays Elettra to provide dedicated measurements selected among the available technologies, granting confidentiality of results and support in problem solving activities;
- Research and Development Projects: the Elettra staff works with the industry using their knowledge and the facilities for products and process co-development;
- Micro Fabrication: Photolithographic fabrication of microelectronic, optoelectronic, micro mechanic and micro fluidic devices;
- Design and Development of advanced scientific instrumentation for the construction of new facilities or laboratory improvements such as: accelerator components, scientific instrumentation, customized software etc.;
- Spin-Offs and New Business Development to promote the use of patented scientific results;
- Consulting and Training of industry personnel.

Services, analysis and measurements performed at Elettra, are illustrated in our catalogue, available upon request, in our promotional video available on You Tube web site and finally in our web site (services section).

The same web site (products section) presents the main groups of devices designed in our facilities and sold throughout the world:

Power Supply Equipment
New families of intelligent (DSP or PC embedded) power supplies, that cover many features (high voltage/current, four-quadrant etc.) with several configurations available. Epics or Tango interface are often already included and custom-built solutions are possible.

Detectors
Photons and charged particles detectors, based on cross delay anodes, multi anodes and centroid finding techniques. 3D information (x,y,time) with spatial and time resolutions in the order of tens of microns and picoseconds are available through many custom-built solutions.

Lab Instruments
Several instruments necessary for typical or extreme applications are available: fast picoameters, multi-point strain gauge, charge pulse amplifiers, ion chambers, pulse generators, RF filters etc. Every tool is intelligent and in some cases “Epics/Tango interface” is already provided.

Accelerator Parts
Elettra, over the years, has acquired wide-ranging experience in developing and realizing accelerators components, including undulators, resonant cavities etc. For the production of Insertion Devices, a spin-off company (Kyma S.r.l.) has been set-up.
How can we help firms be more competitive on the market? How can we promote results in research and translate them into technological products and processes or useful industrial applications with a real impact? Over 100 experts from throughout Europe – including stakeholders from the world of industry, policy-makers, and representatives from the offices for technology transfer of research laboratories and facilities - discussed these issues during the “Technology Transfer and Industrial Relations in Research Infrastructures” conference. The event, organized by the European Association of National Research Facilities (ERF) and Elettra Sincrotrone Trieste, aims to foster a Europe-wide dialogue between two worlds – research and the private sector – which can only find an effective response to the current global crisis through their alliance and constant collaboration.

“The goal of the meeting – explains Marco Marazzi, responsible of Elettra’s technology transfer office – is first and foremost to share our best practices beyond our national borders, and to act in a coordinated manner including with regards to European legislation, which sometimes falls short when it comes to technology transfers and intellectual property. Trieste undoubtedly has much to say in this field, thanks to its exceptional concentration of research centres as Elettra, endowed with offices specifically dealing with technology transfers and collaboration with industry, and to the presence of a leading institution such as Area Science Park: two reference points at the national and international levels”.

Through tangible examples and accounts of successful collaborative efforts in many sectors – from pharmacology to medicine, cosmetics, and electronics – the conference discussed strategic aspects and illustrate operational and networking tools for the research and private sectors, including technological incubators, joint ventures, and technological platforms. One such example is the “Impact Driven” approach that steers the innovation strategies of CERN in Geneva, an institution renowned for having invented the World Wide Web and which is constantly working to identify new technologies which, although they were originally developed for CERN’s particle accelerator, can also have a high socio-economic impacts. Another example is the joint effort between Elettra and Zambon Chemicals, which led to the development of a new protocol to improve the efficacy and safety of pharmaceuticals through the characterization of the active principles used in their formulas. The European Association of National Research Facilities (ERF) represents research facilities built and founded by European countries but open to all researchers from the scientific community, regardless of boundaries and based solely on quality and merit. In order to support and promote Europe’s potential and competitiveness on the global stage, ERF aims to further strengthen its relations with international, national, and local governments, funding agencies and sponsors, other research facilities, the academic and training sectors, the industrial sector, and the citizenry as a whole. For this purpose, over the last several years ERF has organized a series of meetings and discussions in various European countries, focusing on the issues of open access, human capital, energy, and the socio-economic impact of research facilities, and the workshop of the next few days is the latest instalment.
Kyma Srl was established in 2007 as a joint venture between Elettra - Sincrotrone Trieste S.C.p.A. and the industrial companies Cosylab d.d. (Ljubljana) and Euromisure SAS (Cremona).

More than twenty years of experience in design, assembling, characterization and operation of insertion devices at Elettra met the manufacturing capabilities of the industrial partners to build up a world class company for insertion devices design and manufacturing.

The Kyma head office is located in the premises of the Elettra centre, in Area Science Park, while a fully equipped temperature controlled laboratory for assembling and magnetic characterization is situated in the Technology Park of Sežana (SLO), 10 km from Elettra.

The original purpose of Kyma was the realization of the undulators for FERMI, the seeded free electron laser at the Elettra centre.

All the undulators for the FEL-1 and FEL-2 sources have been realized in 2011. Both have been commissioned and are now in full operation.

Next table summarizes the undulators for FERMI.

<table>
<thead>
<tr>
<th>Function</th>
<th>Type</th>
<th>Length</th>
<th>Period</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser heater</td>
<td>LPU</td>
<td>540</td>
<td>40.36</td>
</tr>
<tr>
<td>FEL1 Modulator</td>
<td>LPU</td>
<td>3220</td>
<td>100.0</td>
</tr>
<tr>
<td>Radiator</td>
<td>6 x EPU</td>
<td>2415</td>
<td>55.2</td>
</tr>
<tr>
<td>FEL 2 1st stage</td>
<td>Modulator</td>
<td>LPU</td>
<td>3220</td>
</tr>
<tr>
<td>Radiator</td>
<td>2 x EPU</td>
<td>2415</td>
<td>55.2</td>
</tr>
<tr>
<td>FEL 2 2nd stage</td>
<td>Modulator</td>
<td>EPU</td>
<td>2415</td>
</tr>
<tr>
<td>Radiator</td>
<td>6 x EPU</td>
<td>2400</td>
<td>34.8</td>
</tr>
</tbody>
</table>

Further to the realization of the undulators for FERMI, Kyma is now developing its business on the world market.

A number of contracts have been already awarded:
- one hybrid wiggler for Canadian Light Source, Saskatoon (Canada);
- one Linearly Polarized Undulator for Raja Ramanna Centre for Advanced Technology, Indore (India);
- two Elliptically Polarized Undulators for Pohang Light Source, Pohang (Korea);
- two EPUs (4 movable quadrant Elliptically Polarized Undulators) for Brookhaven National Laboratory (USA)
- development of innovative prototype undulators for SPARX with ENEA (Italy)
- one hybrid planar undulator for the AMOline at ASTRID2 for University of Aarhus - ISA, Institute for Storage Ring Facilities Laboratory Aarhus (Denmark)
- one undulator for the European XFEL Laser Heater for Uppsala University, Uppsala (Sweden)
- an Elliptically Polarized Undulator for the MPI Beamline at PLS-II Storage Ring (Korea)
- one Linearly Polarized Undulator for Huazhong University of Science and Technology (China)
- sixty Phase Shifters for European X-ray Free Electron Laser (Germany)
- compact Adjustable Phase Undulators for Cornell University (USA)
- magnets for Helical Undulators and Mobile Carriage for European Synchrotron Radiation Facility (France)
- two Linearly Polarized Undulators for the AMOS and ARPES beamlines at Indus-2 Storage Ring with compatible Vacuum System at Raja Ramanna Centre for Advanced Technology (India)

How to contact us:

Kyma Srl
S.S. 14 - km. 163.5 in Area Science Park
IT-34149 Basovizza - Trieste, Italy

Tel. +39 040 375 8796
Fax +39 040 375 8209

info@kyma-undulators.eu
http://www.kyma-undulators.eu

Linearly Polarizing Undulator realized by Kyma for FERMI (as installed in the FEL1 undulator chain)

Kyma Tehnologija laboratory in Sežana
During 2012, the company launched an initiative to revise its corporate image, as part of a strategic process that began with a change in the corporate name. These changes were made to strengthen corporate identity at the national and international level and to increase the sense of belonging of the different internal research groups.

In the month of July the Extraordinary Shareholders Meeting approved the change of the corporate name from “Sincrotrone Trieste S.C.p.A.” to “Elettra - Sincrotrone Trieste S.C.p.A.” taking into consideration that the international and national community knows the centre as “Elettra”. The Shareholders Meeting’s resolution also concerned certain modifications and amendments to the company statute to strengthen some of the distinctive points of the corporate mission.

In particular: the exploitation and technology transfer of applied research, the company’s role in supporting and coordinating the activities of the Italian Government and the European Community in the development of international research infrastructure; the in-house training of external technical, scientific, and management staff about the establishment, development, management of complex research and development facilities, reflecting the scientific, technological, and economic evolution of the sectors of interest and in keeping with the relevant national and Community strategic plans.

As a result of the company image revision we hereby present our new logo.
Institutional Events

**ESS, European Spallation Source: agreement renewed**
*(Trieste, December 17, 2012)*

Italy and 16 other countries renewed their Memorandum of Understanding to participate in the pre-construction phase for the ESS – European Spallation Source. The signing ceremony took place at Elettra. The EES – the result of a collaborative effort among mainly EU countries – will be the world’s most powerful neutron source and will equip Europe with the most advanced multi-disciplinary tool for materials research.

*ph. Franco Dreolin*

**ELI, Extreme Light Infrastructure**
*(Brussels, April 11, 2013)*

The Extreme Light Infrastructure (ELI), the world’s first international user facility for laser research, has been established as an International Association during a notarial ceremony in Brussels. When fully implemented in 2017 ELI will contain some of the most powerful lasers in the world. Elettra - Sincrotrone Trieste S.C.p.A. is one of the founding members.

**CERN and Europe join the Middle Eastern synchrotron. INFN and Elettra will take part in the project**
*(May 28, 2013)*

SESAME is the first synchrotron light source in the Middle East. It is currently under construction in Jordan and is scheduled to be completed in 2015, with contributions from countries like: Bahrain, Cyprus, Egypt, Iran, Israel, Jordan, Pakistan, the Palestinian Authority, and Turkey. CERN and European Commission have decided to join this project. Italy will participate through INFN and Elettra by producing some parts of the machine and will be responsible for training staff.
Elettra and IAEA agreement signed at Miur
(Rome, June 19, 2013)
The President of Elettra Carlo Rizzuto and the General Director of IAEA (International Atomic Energy Agency) Yukiya Amano have signed a collaboration agreement in the presence of the Italian Minister for Education, University and Research Maria Chiara Carrozza. The agreement establishes that researchers from IAEA member states can access the facilities of the centre. Within this framework, researchers from emerging countries in particular will get an easier access to X-ray fluorescence techniques using synchrotron light.

CEI Meeting
(Trieste, July 8-10, 2013)
The National Focal Points for Science and Technology meeting has been promoted by the Central European Initiative in order to provide an in-depth analysis of the CEI pilot projects for interdisciplinary research and innovation. The participants were welcomed by Mr. Erik Csernovitz, Assistant National Coordinator for Hungary (on behalf of the CEI Presidency), by prof. Helga Nowotny, President of the European Research Council, by Mr. Wolfgang Streitenberger, spokesman of the EC – DG Regio (on behalf of EU Commissioner Hahn) and by prof. Carlo Rizzuto, President of Elettra, Italian focal point on behalf of the Italian Government.

Inauguration of the experimental station NanoESCA
(July 4, 2013)
The experimental station hosting the NanoESCA spectromicroscope was officially inaugurated, as a result of a cooperation between the Forschungszentrum Jülich GmbH and Elettra.

ph. Alessandra Gianoncelli
Elettra Fellows

Prof. Dietrich Menzel, Prof. Charles S. Fadley and Prof. Ernst Bauer, awarded the title of Elettra Fellow, received a memorial plaque. The title of Elettra Fellow is attributed every year to internationally-renowned scientists and administrators by the Board of Directors of Elettra.

photos Roberto Barnabà

Elettra Fellows

<table>
<thead>
<tr>
<th>Year</th>
<th>Fellows</th>
</tr>
</thead>
<tbody>
<tr>
<td>2012</td>
<td>Helga Nowotny, Robert-Jan Smits</td>
</tr>
<tr>
<td>2011</td>
<td>Hans Chang, Charles S. Fadley, Dietrich Menzel</td>
</tr>
<tr>
<td>2010</td>
<td>John Wood</td>
</tr>
<tr>
<td>2009</td>
<td>Katepalli R. Sreenivasan</td>
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International FEL Award 2013

(New York, August 26-30, 2013)

The prestigious international FEL award is conferred every year to a person who has contributed significantly to the advancement of the field of Free-Electron Laser. The 2013 prize was awarded to Luca Giannessi, Senior Scientist at ENEA and Head of Machine Physics at FERMI, during the 35th International FEL Conference, in New York.
Workshops, Meetings and Schools

Workshop Seeding and Self-seeding at New FEL Sources
(Trieste, December 10-12, 2012)
About 80 scientists from several institutes in the world joined the workshop Seeding and Self Seeding at new FEL sources, hosted by the ICTP at the Adriatico Guesthouse. Spectral quality, brightness and stability of free electron laser amplifiers can be greatly enhanced by seeding this type of lasers with a coherent signal. The workshop critically examined new concepts and long-standing ideas for seeding x-ray FELs.

ph. Roberto Barnabà

Workshop Science@CERIC
(Trieste, December 11-12 2012)
CERIC (Central European Research Infrastructure Consortium) is a distributed research infrastructure, a closely integrated network of laboratories, with the aim to maximize the quality in research. During the Science@CERIC workshop the experts led to the formulation of a number of possible research projects in the fields of life and materials sciences, which can use the large potential offered by CERIC.

ph. Roberto Barnabà

Fonda-Fasella 2012 award to Michela Fratini
(Trieste, December 12, 2012)
The Fonda-Fasella prize is awarded to a young researcher who has obtained important results while working at Elettra. This year the winner was Dr. Michela Fratini, from the “Centro Studi e Ricerche Enrico Fermi” (Rome), who presented the paper “Manipulation and Control of Oxygen interstitials in a Superconductor cuprate, La2CuO4 + y, using X-ray diffraction”.

ph. Roberto Barnabà
Nuclear power in post World War II Italy: the Ippolito affair
(Trieste, November 15-16, 2012)
The national conference “Nuclear power in post World War II Italy. Research, culture, politics” was organized by Elettra and the Graduate School in Humanities of the University of Trieste. The conference ended with a panel discussion about “Felice Ippolito and the Italian controversy on nuclear power.”

3rd Tutorial of Advanced Synchrotron Techniques at Elettra
(Trieste, March 18-19, 2013)
Elettra hosted the third “Tutorial of Advanced Synchrotron Techniques”, with the participation of undergraduate and PhD students from the Montanuniversität Leoben and the Technical University of Graz. The latter is managing the SAXS beamline at Elettra since October 2012.

National Fire Corps drill at Elettra
(Trieste, April 4-5, 2013)
The Command of Trieste of National firemen Corps hosted a drill for Nuclear and Radiological (NR) advanced nuclei. Elettra was one of the locations chosen for the drill. The NR teams, coming from Trieste, Milan and Pavia, had to simulate emergency actions related to nuclear and radiological risk with the support of the radioprotection experts of the research centre.
“Invisible” to protect Manerbio drachmas
(Brescia, April 4, 2013)
Elettra took part to the meeting “New technologies for ancient relics: the example of Manerbio drachmas”. Materials science and related technologies can answer many needs in the field of cultural heritage. Santa Giulia Museum in Manerbio, near Brescia, collaborated with Elettra in order to inventory relics and artifacts (like the ancient celtic coins in Manerbio), and to mark them with an invisible stamp. All thanks to synchrotron light.

International Workshop HG2013 (Trieste, June 3-6, 2013)
The “International Workshop on Breakdown Science and High Gradient Technology” (HG2013) was organized for the first time by Elettra, in collaboration with CERN (Geneva), SLAC (USA) and KEK (Japan). More than 70 scientists took part to the meetings, exchanging knowledge in the field of high frequency and high gradient acceleration. The workshop was also aimed to promote collaborations and a wider use of high-gradient technology.

12th School on Synchrotron Radiation (Grado, September 16-27, 2013)
“Synchrotron Radiation: Fundamentals, Methods and Applications”. This the title of the 12th edition of the school organized by SILS (Italian Society of Synchrotron Radiation) and Elettra Sincrotrone Trieste. Over 40 young graduates in Physics, from all over the world, joined the school to meet the most qualified experts and to do practical training and data analysis sessions at Elettra.
Trieste Next 2013 and Researchers’ Night 2013: large participation at the Elettra stand

The second edition of Trieste Next, promoted by the Municipality of Trieste, the University of Trieste and NordEstEuropa Editore, was held jointly with the European event Researchers’ Night. Over 35,000 people attended the three-day event: people of all ages visited the exhibitions and events around Piazza Unità, the main town square.

The stand of Elettra attracted many visitors, and was constantly animated by the enthusiastic presence of researchers and technicians who presented the activities of the centre. Visitors enjoyed “Fold it!”, a videogame that works like a puzzle and teaches to fold proteins correctly, and a quiz game about Physics and the adventures of a fictional 007 secret agent/physicist. A very active audience took part to the panel discussion “This strange thing we call H2O”.

Elettra has taken part in the photo exhibition “Around the world in 80 clicks”

ph. Roberto Barnabà
Within the project “Adopt Srebrenica”, to which the Municipality of Trieste is operating since 2005, a group of youngsters from the Bosnia and Herzegovina town was welcomed in Basovizza by the researchers of Elettra and taken on a guided tour of the two lightsources.

*ph. Roberto Barnabà*
TECHNOLOGY FOR RESEARCH

Power Supply Equipment
New families of intelligent (DSP or PC embedded) power supplies, that cover many typologies (high voltage/current, four-quadrant etc.) and configurations are forthcoming. Epics or Tango interface are often already present and custom-built solutions are possible.

Detectors
Photons and charged particles detectors, based on cross delay anodes, multi anodes and centroid finding techniques are steadily developed. 3D information (x,y,time) with spatial and time resolutions in the order of tens of microns and picoseconds are available through many custom-built solutions.

Lab Instruments
Several instruments necessary for typical or extreme applications are available: fast picoammeters, multi-point strain gauge, charge pulse amplifiers, ion chambers, pulse generators, RF filters etc. Every tool is intelligent and in some cases “Epics/ Tango interface” is already provided.

Accelerator Parts
Elettra, over the years, has acquired great experience in developing and realizing accelerators components i.e undulators, resonant cavities etc. While for the production of Insertion Devices, a specific spin-off company has been set-up, for all the other components Elettra will provide them on request.

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Kyma was established in 2007 as a joint venture between Elettra - Sincrotrone Trieste S.C.p.A. and the industrial companies Cosylab d.d. (Ljubljana, SLO) and Euromisure Sas (Cremona, I). More than twenty years of experience in design, assembling, characterization and operation of insertion devices at Elettra met the manufacturing capabilities of industrial partners to build up a world class company for insertion devices design and manufacturing.

The Kyma head office is located in the premises of the Elettra centre, in Area Science Park, while a fully equipped temperature controlled laboratory for assembling and magnetic characterization is situated in the Technology Park of Sežana (SLO), a town just 10 km from Elettra.

A further lab for mechanical design, assembly and characterization is operating at Euromisure. The competencies and resources available at Kyma allow the realization of top performing insertion devices at competitive prices and unexpectedly short delivery times.
AREA Science Park is recognized as the main and more experienced multi-sector science and technology park in Italy and as an effective regional innovation system. The park extends on 55 hectares surface and has more than 90,000 sqm of equipped laboratories, offices and service structures established in two campuses on the hills overhanging Trieste and in one campus in Gorizia, in the Friuli Venezia Giulia Region that is part of the well known Italian North-East area.

Presently, AREA Science Park consists of almost 80 national and international R&D organisations, that include public research institutions, private R&D and innovation centres, knowledge-based companies. The personnel is over 2400 units.

AREA Science Park is a research-driven cluster with multi-disciplinary features. The basic technology and business sectors are:

✓ life sciences and biomedicine
✓ physics, materials and nanotechnologies
✓ electronics, informatics and communication
✓ environment and energy.

AREA Science Park is managed by a national research institution, the Consorzio per l’AREA di Ricerca Scientifica e Tecnologica di Trieste (briefly AREA), that operates under the vigilance of the Italian Ministry of University and Research.

The mission of AREA is:
✓ to develop the park as a regional innovation system in the national and international scenario
✓ to contribute to the competitiveness of regional industry through technology transfer, innovation management, management of R&D programmes and knowledge-intensive enterprise creation
✓ to increase the regional innovation level through training and mobility program
✓ to develop initiatives of capacity building in Europe and abroad based on strategic planning for sustainable development, innovation management and technology transfer.
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