Program & Book of Abstracts
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November 27
14:00-15:00 Registration
15:00-16:00 WELCOME CEREMONY
15:00-15:45 Opening ceremony Prof. Massimo Innocenti, University of Florence
15:45-16:00 Technical introduction to the School Prof. Nicola Cioffi, University of Bari
16:00-17:40 SESSION I, chairperson: Prof. Debora Berti, University of Florence
16:00-16:40 A unitary preliminary vision of the processes underlying surface characterization tools, part I. Prof. Gaetano Granozzi, University of Padua
16:40-17:00 Coffee break
17:00-17:40 A unitary preliminary vision of the processes underlying surface characterization tools, part II. Prof. Gaetano Granozzi, University of Padua
17:40 End of Session
17:40-18:40 Meeting of CHESS Scientific Committee (only for the SC members)
20:30 Welcome reception

November 28
8:30-9:30 Registration
9:30-13:10 SESSION II, chairperson: Prof. Antonino Martorana, University of Palermo
9:30-10:10 SPR Spectroscopy Prof. Giuseppe Spoto, University of Catania
10:10-10:50 ATR-IR Spectroscopy Dr. Emilia Bramanti, CNR Pisa
10:50-11:30 Raman Spectroscopy Prof. Giulietta Smulevich, University of Florence
11:30-11:50 Coffee break
11:50-12:30 ex-situ and in situ Scanning Probe Microscopies Prof. Massimo Innocenti, University of Florence
12:30-13:10 SIMS Dr. Stefano Caporali, University of Florence
13:10-15:00 Lunch
15:00-18:40 Session III, chairperson: Dr. Luca Gregoratti, Elettra, Trieste
15:00-15:40 XPS -fundamentals Dr. Marzia Fantauzzi, University of Cagliari
15:40-16:20 Progresses in XPS and AES for nano-analysis Prof. Antonella Rossi, University of Cagliari
16:20-16:40 Coffee break
16:40-17:20 XRF Dr. Francesco Di Benedetto, University of Florence
17:20-18:00 SEM Dr. Maria José Irene Lo Faro, CNR, Messina
18:00-18:40 RBS Dr. Maria José Irene Lo Faro, CNR, Messina
18:40 End of Session
November 29
8:30-9:00 Registration
9:00-13:10 Session IV, chairperson: Prof. M. Innocenti, University of Florence
9:00-9:50 Introduction to synchrotron radiation and overview on synchrotron radiation facilities
Prof. Antonino Martorana, University of Palermo
9:50-10:40 Analysis modes at a synchrotron facility Dr. Luca Gregoratti, Elettra, Trieste
10:40-11:30 FELs: principles and applications in chemistry Dr. Oksana Plekan, Elettra, Trieste
11:30-11:50 Coffee break
11:50-12:30 X-rays to determine structure and morphology of surfaces Dr. Roberto Felici, CNR-SPIN, Roma
12:30-13:10 X-rays to study reactions and processes at surfaces Dr. Francesco Carlà, ESRF, Grenoble
13:10-15:00 lunch
15:00-18:40 Session V, chairperson: Dr. Roberto Felici, CNR-SPIN, Roma
15:00-15:35 EXAFS- XANES/micro-XANES Inverse Photoemission, part I Dr. Maddalena Pedio, CNR – IOM, Trieste
15:35-16:00 FEXRAV Dr. Alessandro Minguzzi, UNIMI, Milano
16:00-16:40 EXAFS- XANES/micro-XANES Inverse Photoemission, part II Dr. Maddalena Pedio, CNR – IOM, Trieste
16:40-17:00 Coffee break
17:00-17:40 Photoemission spectroscopies/microscopies + NAPXPS. Dr. Luca Gregoratti, ELETTRA, Trieste
17:40—18:40 Poster session (including selection of the best poster)
18:40 End of Session
20:30 Social Dinner

November 30
09:30-13:00 Session VI chairperson Prof. Nicola Cioffi, University of Bari
09:30-10:10 How to have access to a synchrotron facility Dr. Roberto Felici, CNR-SPIN, Roma
10:10-10:50 Examples of research projects and cases of study Dr. Andrea Giaccherini, University of Florence
10:50-11:10 Coffee break
11:10-11:50 Electron Microscopies combined with spectroscopies and/or microanalysis (EDX, EELS, etc.) Dr. Alessandro Lavacchi, CNR, Firenze
11:50-12:30 Scanning probe microscopy techniques for materials characterization Dr. Massimiliano Cavallini, CNR, Bologna
12:30-13:00 Final exam (warmly suggested, but not mandatory!)
13:00-13:10 CONCLUDING REMARKS AND CLOSING CEREMONY
Abstracts
Plasmonic Effect of Metal Nanoparticles on Wide-Band Gap Metal Oxide Nanowires

Mojtaba Gilzad Kohan¹*, Isabella Concina¹ and Alberto Vomiero¹

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In the field of renewable energies, solar cells (SCs) based on nanowires (NWs) are of great interest due to their outstanding optical and electronic properties. Specifically, NWs composed of metal oxides (MOs), with desirable single crystalline structure, present remarkable optical, charge transport and waveguide properties that can be productively exploited in photovoltaic (PV) systems with high photo-conversion efficiencies (PCE). In addition, integrating plasmonic metal nanoparticles (NPs) such as silver, gold and copper NPs on MOs semiconductor NWs, can increase the performance in SCs owing to plasmon resonance effect of noble metal NPs [2].

In this work, vertically aligned ZnO and TiO₂ NW arrays were grown on fluorine-doped tin oxide (FTO) conductive glass substrates via hydrothermal method at low temperature. The plasmonic NPs were synthesized by wet chemistry, and finally decorated on the NW films by electrophoretic deposition.

The impact of metal NPs loaded on the ZnO and TiO₂ NWs substrates was studied by means of UV-vis spectroscopy and Photoluminescence (PL) spectroscopy. The absorbance spectra of individual NPs were recorded. Remarkably, the reflectance spectra of produced samples presented an enhancement in light absorption of the substrates at the corresponding plasmonic region of specific NPs which were deposited on the ZnO and TiO₂ NWs. The optical properties of the as grown ZnO NWs films decorated with Ag NPs (I) in direct contact with substrate and (II) in presence of an Al₂O₃ insulating spacer layer have been analyzed. One of the main reasons behind employing the Al₂O₃ layer in between NPs and NWs, was to avoid direct contact of plasmonic NPs and NWs substrate to investigate one of the typical behaviors of plasmonic materials called localized surface plasmon resonance (LSPR). Both systems exhibited an enhancement in the UV band-edge emission from the ZnO when excited at 325 nm. The observed results suggested that the ZnO and TiO₂ NWs decorated with plasmonic nanoparticles can boost the optical properties of MOs NWs substrates and hence effectively enhance the separation of photoexcited electron-hole pairs for photo-conversion applications.

References:
FEXRAV applied to the study of palladium nanoparticles' surface in fuel cells

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To fight the inexorable increasing of energy demand and pollution, it is crucial to develop highly efficient and clean energy conversion devices. In fact, current technologies have a bad impact on the environment or require great energy and raw material costs [1]. A winning approach is the controlled conversion of chemical energy to electricity from renewable sources [2]. For this reason, devices such as fuel cells are very interesting. In particular, ADAFCs (Alkaline Direct Alcohol Fuel Cell) are very promising because, in addition to producing high-power electrical energy and efficiency, their products, like acetates, are industrially interesting.

These devices need to be understood in deep to improve their extrinsic energy efficiency. To reach this goal Fixed Energy X-ray Absorption Voltammetry technique have been used. FEXRAV (Fixed Energy X-ray Absorption Voltammetry) and represents an innovative, fast and easy [3] method for the in situ and in operando X-ray absorption analysis at a fixed energy during a cyclic voltammetry and is particularly suitable for the investigation on the electrodic surface for heterogeneous catalytic reactions [4].

For the first time FEXRAV have been used to study the behavior of palladium nanoparticles supported on carbon in KOH solution with various organic fuels. By results, it is possible to detect and quantify the percentage of oxide on the surface of the catalyst, the maximum overpotential before the poisoning of the catalyst and its loss in function of time; even some information on the reaction mechanisms could be obtained.

References:
Nano-tetragonal zirconia for catalytical purpose

Alessia Giordana1,*, Elisabetta Bonometti1, Eliano Diana1, Lorenza Operti1 and Giuseppina Cerrato1
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Zirconia (ZrO2) tetragonal nanoparticles have been obtained by a quick and green procedure assisted by microwave radiations. ZrO2 was prepared by sol-gel method starting from Zr propoxide solution, ethanol as solvent and HNO3 as catalyst: the gel obtained was dried in a microwave oven and then has been calcined in microwave oven using graphite as susceptor. The product obtained so far is highly crystalline as confirmed by different experimental techniques, such as Raman and FT-IR spectroscopies and X-Ray diffraction (XRD). Work is in progress to determinate both BET specific surface area and porosity, as well as the investigation of the morphology by means of HR-TEM. Zirconia is a very versatile material which has found applications in many technologies, such as solid oxide fuel cell, oxygen sensor, solid acid catalyst and catalyst support to disperse various noble and transition metals for distinct catalytic. Obtained material will be tested as catalyst for biomass valorization.

On the left Raman spectrum, on the right comparison between experimental XRD and PDF [00-152-5706], t-ZrO2.
Synthesis and Characterization of N-Doped Semiconductors for Photocatalytic Applications

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As a consequence of the rapid growth of population in urban areas, water use and reuse has become a major concern, leading to an urgent imperative to develop effective and affordable technologies for wastewater treatment. Traditional methods for wastewater treatment are usually based on physical and biological processes but unfortunately, some organic pollutants, classified as bio-recalcitrant, are not biodegradable. In this way heterogeneous photocatalysis may become an interesting water treatment technology to remove organic pollutants not treatable by conventional technique. Photocatalysis, also called the “green” technology, represents one of the main challenges in the field of treatment and decontamination of water and air because it is able to work at ambient temperature and atmospheric pressure. Heterogeneous photocatalysis is a catalytic process that uses the energy associated to a light source to activate a catalyst with semiconducting proprieties. The most common used photocatalyst are TiO₂ and ZnO [1]. It is able to oxidize a wide range of toxic organic compounds into harmless compounds such as CO₂ and H₂O. Due to the value of their band-gap energy, about 3.2 eV, they are effective only under irradiation of UV light [2]. This is a technological limitation when aiming at implementation of large scale sustainable “green” technologies with renewable energy sources such as solar light. The main research objective is the increase the photocatalytic performances of TiO₂ and ZnO through the doping of their crystalline structure with non-metal ions (nitrogen) that reduce the band-gap making possible the fruitful absorption of the visible light. The synthetized doped sample were characterized by XRD analysis, BET, Raman and UV-Vis spectroscopy. Finally the photocatalytic performances of the doped samples in the removal of model organic pollutants were analyzed and compared.

References:
Electrodeposition of bismuth's chalcogenides thin films

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In recent years, the scientific community has shown a strong interest for thin films of metals and semiconductors materials, that can be used for both electronic and photovoltaic devices. Good candidates, for both these applications, are transition metal and post-transition metal chalcogenides, which is why Bismuth Selenide Bi₂Se₃ was synthesized and studied in this specific study [1].

The possibility to produce thin films with the electrodeposition EALD technique allows to obtain monocrystalline semiconductor materials with minimum percentages of defects and of pollutants, at standard temperature and pressure conditions [2]. Through this technique it’s possible to obtain a wide range of semiconductors of industrial interest, exploiting the phenomenon of the UPD.

Electrochemical studies have been conducted to determine the potential UPD of Bismuth and Selenium on the Ag(111) electrode, limiting the electrodeposition to the surface and obtaining with this procedure thin films under the control of composition, morphology and structure.

The work is continued by the electrodeposition of alternate layers of Bismuth and Selenium, by the solutions of SeO₂⁻ in ammoniacal buffer and Bi³⁺ in ammoniacal buffer + EDTA, always on the electrode of Ag (111), thus creating the binary compound Bi₂Se₃.

Through stripping voltammetry, it was possible to quantify the charge deposited of Selenium UPD and to have a qualitative feedback on the actual deposition both of Bismuth and Selenium. Finally, it was possible to analyse both the chemical composition and the morphology of the Ag(111)/Se/Bi and Ag(111)/Bi samples by X-ray photoelectron spectroscopy (XPS) and by using the Scanning Electron Microscope (SEM).

References:
A combined FTIR and SS MAS NMR characterization of acid sites in hierarchical architectures for Beckmann rearrangement

Chiara Ivaldi1,*, Ivana Miletto1, Stephanie Chapman2, Robert Raja2, Leonardo Marchese1 and Enrica Gianotti1

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Hierarchical H-ZSM-5 and SAPO-34 catalysts have been obtained following both “bottom-up” and “top-down” approach. The nature, strength and accessibility of the acid sites present in the hierarchical materials were elucidated by means of a fine physical-chemical characterization using FTIR spectroscopy of adsorbed molecules together with SS MAS-NMR.

In this contribution, a post-synthetic desilication strategy in alkali media was followed to achieve hierarchical H-ZSM-51 and a bottom-up approach to obtain hierarchical SAPO-342. Both H-ZSM-5 and SAPO-34 possess acid active sites and are widely used as acid heterogeneous catalysts. In particular, a novel, facile, bottom-up approach was used to synthesize a hierarchical SAPO-34 acid catalyst that mitigates the use of sophisticated surfactants, instead using ordered mesoporous silica (MCM-41) with CTAB as both silicon source and mesoporogen. To get information on the nature, strength and the accessibility of the acid sites in the hierarchical zeotype catalysts, a fine physical-chemical characterization using FTIR spectroscopy of adsorbed probe molecules together with SS MAS-NMR was performed. In addition, structural and textural properties of the hierarchical zeolites were also explored by means of XRD and volumetric analyses. In this study, CO was used to assess the acidic properties of the hierarchical zeolites and bulky basic molecules as pyridine, 2,4,6-trimethylpyridine and 2,6-di-tert-butylpyridine, that cannot enter the micropores, were used to get information on the enhanced accessibility of the active sites. Probe-based studies are particularly pertinent in catalysis for establishing structure-property relationships.

The hierarchical materials showed superior activity in the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam (precursor of Nylon-6) with respect to the parent microporous systems. This superior catalytic activity can be explained by the overcoming of the diffusion constraints due to the introduction of mesoporosity, well documented by the volumetric analysis and by the enhanced accessibility of active sites.

References:
Development of a biosensing antifouling platform for DNA detection

Noemi Bellassai\textsuperscript{1,2,*}, Almudena Marti Morant\textsuperscript{3}, Jurriaan Huskens\textsuperscript{3} and Giuseppe Spoto\textsuperscript{2,4}

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Antifouling surfaces are required for many biotechnological applications to prevent the non-specific protein/cell adhesion and select biological targets, such as cancer biomarkers, in complex natural media (e.g., blood) \cite{1}. It has been suggested that a nanoscale homogenous mixture of balanced charged groups from polyzwitterionic systems is the key to control the non–fouling properties \cite{2,3}. To address this problem, a new approach of the nanostructured zwitterionic polymer is performed using the combination of a cationic polyelectrolyte and an anionic oligopeptide structure. The polymeric system investigated consists of a poly (L-lysine) (PLL) backbone grafted with maleimide-NHS ester chains in different percentage (y\%) of maleimide (PLL – Mal\textsubscript{y\%}, from 26\% to 13\%). The anionic oligopeptide structure included five glutamic acids (E) and one cysteine (C) (oligo CEEEEE) has been attached to a PLL – Mal\textsubscript{y\%} polymer through the thiol – maleimide “click” reaction. The final zwitterionic layer has overall charge neutrality, as a result of the balance between the positive charges of PLL – Mal\textsubscript{y\%} and the negative charges of the oligo CEEEEE. The antifouling surfaces were characterized by Water Contact Angle and Polarization Modulation Infrared Reflection-Absorption Spectroscopy (PM-IRRAS). Data analysis indicated the successful formation of the layers. Their antifouling properties have been assessed in adsorption studies using Quartz Crystal Microbalance with Dissipation (QCM-D) using Bovine Serum Albumin (BSA) aqueous solutions as the standards. The best antifouling properties for PLL-Mal\textsubscript{y\%} have been obtained when 26\% and 22\% of maleimide were used with gold and silicon oxide sensors, respectively. Furthermore, preliminary data were also collected for PLL – Mal\textsubscript{y\%} functionalized surfaces using diluted (5\%, 10\%, 33\%) human plasma. The useful strategy for the functionalization of PLL – Mal\textsubscript{y\%} with oligo CEEEEE could be employed for the synthesis of different antifouling layers. For instance, thiol-modified oligonucleotide probes (such as DNA or PNA probe sequence) could be immobilized on PLL – Mal\textsubscript{y\%} – CEEEEE films to develop a versatile polymer with effective antifouling and detection properties.

References:
Studies on the Effect of Nanoparticles on Laser Ablation Processes

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Laser Induced Breakdown Spectroscopy (LIBS) is an analytical technique based on the emission by atoms in Local Thermal Equilibrium, inside a plasma created, after the interaction between a sample and a Laser. Thanks to some of its characteristics, like easy or no sample preparation, simple set-up and high sensitivity, its use and interest is wide spreading in the industrial and academic sectors. Starting from the research of De Giacomo et al. [1], the aim of this work was to increase our knowledge about Nanoparticle-Enhanced LIBS (NELIBS), a modified version that results in an amplified signal when metal NPs are poured onto the specimen.

In the first part of this work, some fundamental results from other works were reproduced. Among these, worth citing are the increasing in the sensitivity seen by comparing calibration curves for the same element with both LIBS and NELIBS.

The second part of this work was focused on having a bigger insight in the differences about the plasma created by the two different techniques. This was achieved applying for the first time a numerical algorithm, called Abel Inversion [2], to imaging measurements made on the whole plasma plume or on single atomic lines. This brought to 3D images with information about emissivity in every point of the image, giving the chance to evaluate the emitting distribution in the whole plasma body. This was done in different temporal frames in order to study plasma evolution.

These results confirmed initial hypotheses: plasma from NELIBS experiments appeared brighter and wider; however, they were far from being representative of the whole phenomenon.

References:
Characterization of ternary and binary ultra-thin films semiconductors deposited by E-ALD
Francesca Russo1,*
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Chalcogenide nanomaterials are very interesting candidates for solar energy conversion and photovoltaic, but CdSe and CdTe display high toxicity and are unfavorable for the large scale exploitation. Thus, scientific community is now focusing attention on new compounds based on economic and low-environmental impact elements such as Cu, Sn, Fe and Zn. Electrodeposition is known as a low-cost technique for the direct growth of compound semiconductors in the form of thin films. Nowadays the main outcome of the Electrochemical Atomic Layer Deposition (E-ALD) technique is the growth of binary and ternary ultra-thin films exploiting several consecutive and alternated surface limited electrodepositions of atomic layers of different elements.[1] Among these compounds, CuₓZnᵧS and CuₓS films, grown on Ag(111) single crystals, are expected to be suitable for photovoltaic applications. Open questions about the structure and the growth process of the films can be addressed exploiting an operando SXRD characterization, as reported for the CuₓZnᵧS film. On the other hand a morphological and compositional characterization is also important to determine the main properties of the films and confirm the results obtained by operando SXRD, as shown for the CuₓS film. The study carried out on the ternary film led to a qualitative interpretation of the growth mechanism, pointing out that the presence of Zn could lead to the growth of a strained Cu₂S-like structure and the growth of thread-like structures is probably driven by the release of the stress.[2] The morphological and compositional study carried out on the binary film of CuₓS shows that the surface of the film is very homogeneous and that the film has a Cu/S ratio close to two, confirming the results obtained by the structural SXRD characterization, which pointed out the presence of only a Cu₂S (chalcopyrite) phase.[3] Thus, is possible to state that combining dimensional and compositional control the E-ALD process allows to deposit ordered thin films semiconductors, representing a promising technique for overcoming the current issues of the photovoltaic technology.

References:
Characterization of new composites for food-packaging applications

Margherita Izzi1,*, Maurizio Clemente1, Maria Chiara Sportelli1,2, Annalisa Volpe2, Rosaria Anna Picca1, Amalia Conte3, Matteo Alessandro Del Nobile3, Antonio Ancona2, Nicola Cioffi1

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In the last decades, the application of metal and metal oxides in the form of nanostructured antimicrobials has attracted the interest of scientists and technologists. Particular attention has been addressed to Cu- and Ag-based nanoantimicrobials1, as assessed by a large amount of reports about their synthesis and characterization2. The development of bioactive metals with controlled ion release, which allows having a significant antimicrobial activity associated with low toxicity to humans, is one of the leading challenges in the scientific community. Nanoantimicrobials are able to release metal ions in solution with defined kinetic profiles, which can slow down or inhibit bacterial growth3. In our recent studies, we developed and deeply characterized many different nanoantimicrobial systems, ranging from Ag- and Cu-modified textiles4 to bioactive food packaging5. These materials have opened new horizons in the searching of alternative routes to fight bacterial resistance towards conventional antibiotics and disinfecting agents. Furthermore, they showed no significant leaching of potentially toxic whole nanoparticles into contact media, which makes them human safe. Here we produced bioactive Cu- and Ag-based nanocolloids by Laser ablation synthesis in solution (LASiS). These nanocolloids, synthetized in organic media, were included as nanophases into a polymer (like polyethylene oxide), to obtain composite materials combining physicochemical properties of both components. In this study, transmission and scanning electron microscopies allowed us to study nanocolloids morphologies, while UV-Vis provided us information on bulk chemical characterization. X-ray photoelectron spectroscopy was exploited to evaluate chemical speciation and elemental composition of both pristine nanoparticles and final composite materials. Moreover, electrothermal atomic absorption spectroscopy was used to investigate metal ion release from nanocomposite surfaces. Finally, bioactivity tests on target food spoilage microorganisms were performed.

References:
Optimizing the Electrodeposition Protocol of Enantioselective Inherently Chiral Electrode Surfaces: a Multi-Technique Investigation

Serena Arnaboldia, Patrizia Mussinia, Claudia Malacridaa, Mirko Magnia

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We have recently introduced [1-2] "inherently chiral" enantiopure electrode surfaces of outstanding chirality manifestations, including circularly polarized luminescence, reversibly potential-driven circular dichroism, and large potential differences for the enantiomers of chiral probes in voltammetry experiments performed on such surfaces.

The outstandingly powerful “inherent chirality” concept implies a molecular structure where the stereogenic element does not consist in an isolated stereocenter or an external chirality source, but originates from a tailored torsion in the whole main backbone endowing the molecule with its key functional property (here electroactivity). A key issue is now to investigate the enantioselection mechanism and to optimize the experimental deposition protocol of our inherently chiral surfaces. For both aims it is important to study thickness, regularity and homogeneity of the chiral oligomer films as a function of the experimental conditions.

We have started a systematic profilometry study correlated to electrochemical impedance spectroscopy measurements of the oligomer films obtained by carefully controlled electrodeposition, varying one by one different experimental parameters. The study is also important to properly compare enantioselection by films prepared from different inherently chiral monomers, including e.g. bisindole and tetrathiahelicene ones.

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References:
Probing the Correlation between Pt-Support Interaction and Oxygen Reduction Reaction Activity in Mesoporous Carbon material modified with Dichloro(1,10-phenanthroline)platinum(II)

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The increment of Pt catalytic activity catalyst for oxygen reduction reaction (ORR) in PEMFC can be pursued according to two routes: i) Pt/support interaction ii) Pt alloyed with another transition metal. In this paper we analyzed the first one by exploring a novel one step synthesis of Pt and nitrogen doped mesoporous carbon catalyst by using a platinum precursor bearing a nitrogen containing ligand such as 1,10-phenanthroline or 2,2'-bipyridine. The synthesis would allow to keep the metal NPs as much close as possible to the nitrogen domains. This would allow us to examine whether the electronic interaction between nitrogen and the metal nanoparticles can increase the mechanical stability and the catalytic activity of metal NPs.

Pt NPs of average size of 2–5 nm were successfully synthesized by solid state thermal reduction on a commercial carbon. XPS analysis confirmed that during the treatment the ligand degrades and the nitrogen in embedded in the mesoporous carbon structure obtaining a surface modification of the carbon support, preserving the bulk conductivity and thermal stability (fig. 1a). In catalyst in which XPS showed high Pt-Nitrogen interaction, the electrochemical characterization revealed an increased catalytic activity towards ORR notwithstanding the low Pt loading (fig. 1b).

Figure 1. a) N 1s XPS peak comparison between the doped carbon support and the catalysts obtained by using the 1,10-phenanthrolina b) LSVs recorded at scan rate of 20 mV s-1 in O₂-saturated 0.1 M HClO₄ at 25 °C, rotation rate 1600 rpm

References:
XPS characterization of thin layered semiconductors grown by electrochemical atomic layer deposition (E-ALD)

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Recently, two-dimensional semiconductors have attracted considerable interest as promising materials for the development of (opto)electronic devices and photovoltaic cells, reduced defects states on the surface and high carrier mobility [1]. For example, low-cost inorganic thin film solar cells based on inexpensive, non-toxic and abundant elements could be fabricated [2]. In this context, chalcogenides are attracting interest due to their good performance and potential efficiency in the conversion of solar energy [2-4]. These materials are generally prepared by using high temperatures and vacuum methods. An alternative non-vacuum and room temperature approach is represented by a particular electrochemical technique, known as electrochemical atomic layer deposition (E-ALD) [5]. The growth of thin films by E-ALD consists of the alternating underpotential deposition (UPD) of the elements of interest [2, 5-6]. Recently, the E-ALD preparation of MoSe₂ films by alternating the electrochemical deposition of Se and Mo onto Ag(111) substrates has been investigated at the University of Florence, and the resulting materials have been characterized in Bari by X-ray photoelectron spectroscopy (XPS) [2, 6]. Indeed, XPS analysis can provide a quantitative determination of the surface elemental composition and information about the chemical environment associated to the identified elements. In this communication, XPS results obtained on Mo/Se layers grown by E-ALD is presented and correlations between surface composition and deposition conditions are drawn.

References:
In Situ Study of the Catalytical properties of Pd-Au surfaces growth using Surface Limited Electrodeposition Methods

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Platinum is nowadays considered as the best catalyst for many anodic and cathodic reactions in fuel cells, but its low abundance and high cost pose a limit in its usage in such devices. Particularly regarding the alcohol electrooxidation process in direct alkaline alcohol fuel cells (DAFC), much effort has been undertaken to substitute this metal with cheaper and more abundant other ones. Palladium (which shares with platinum a similar catalytic activity towards alcohol electrooxidation) is considered a viable substitute for the anodic compartment in DAFC, but its main limit resides in the deactivation process (oxidation of the metal) that occurs during the cell duty cycle. With the aim to study this phenomenon via XAS experiments, different catalytically active bimetallic Au-Pd electrodes were prepared first depositing submonolayers of a metal (Cu,Pb) on Au (111) polycrystalline surfaces, using the under potential deposition (UPD) phenomenon, and then substituting the metal with palladium exploiting galvanic replacement. Particular effort has been made to produce cheap and reproducible gold electrodes on which to perform the deposition and substitution processes. These surfaces were prepared to perform physical vapor depositions (PVD) of different metals on microscope slides. Various heat treatment processes on the electrodes were also tested, to permit the rearrangement of the upmost gold layer to a (111) surface. The obtained catalytic substrates were then tested in respect to the electrooxidation of various alcohols during cyclic voltammetry studies. Their surfaces were also analyzed using atomic force microscope (AFM) and X-ray photoelectron spectroscopy (XPS) to obtain both morphological and compositional data. The obtained surfaces were finally tested during an operando experiment, in which the grazing incidence x-ray absorption spectroscopy (GIXAS) was combined with the Fixed Energy X-Ray Absorption Voltammetry technique. These experiments were performed at the European Synchrotron Radiation Facility in Grenoble, to study the deactivation of palladium during voltammetric scans.
Surface characterization of enzymes exposed to atmospheric plasmas

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Nowadays immobilization of enzyme on general substrate for biosensing application and to obtain their stabilization is a crucial point. Plasma Enhanced Chemical Vapor Deposition (PECVD) at atmospheric pressure is a powerful and innovative method that allows the deposition of a thin layer of polymeric materials. The polymerization is realized in mild conditions (moderate temperature, dried state, reduced ion bombardment) and this permits the immobilization of an enzyme or a biological molecule without altering their functionalities.

In this work two different enzymes (Tyrosinase and Glucose Oxidase) were immobilized with a two-step procedure in which a drop of the solution containing enzyme is first allow to dry on a glass substrate. Successively a polyethylene-like coating is deposited by PECVD at atmospheric pressure by the use of a helium/ethylene feed gas mixtures. In order to evaluate possible effects exerted from plasma on the enzyme structure and functionality both the two enzymes were exposed to a helium and helium/oxygen feed gas mixture. These exposed enzymes represent the control samples.

Surface analysis measurements of enzymes have been performed before and after the enzymes exposure to different plasmas by means of X-ray photoelectron spectroscopy (XPS) and White Light Vertical Scanning Interferometry (WLVSI) in order to study the modifications induced by plasma exposure at the outmost surface layers of the materials. Both XPS and WLVSI results suggest a certain etching of enzyme deposits exposed to a helium/oxygen fed plasma, while minor changes were observed when the plasmas is fed only by helium.
Surface Modification of Polymeric Electrospun Mats with Biomolecules to Obtain Smart Affinity Membranes

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In the last decades much efforts have been put in the study of polymeric surface modification by mean of immobilization of bioactive compounds such as drugs, enzymes and antibodies. Surface modification with molecules targeting biological functions, through surface target chemistry, allows to obtain smart devices suitable for many different applications within medical diagnostics, drug delivery, tissue engineering and affinity membranes. In particular, the possibility to obtain smart materials capable to selectively recognize specific group of cells, is of extreme interest. These cell-specific affinity membrane can be exploited to selectively capture cells from complex mixture through antibody-antigen recognition allowing the diagnosis of specific diseases or the selection and purification of specific cell population. Electrospinning is a widely recognized technique that allows to obtain, starting from either natural or synthetic polymers, nonwoven mats made of fibers with sub-micrometric diameter and characterized by high surface to volume ratio. Electrospun mats can be obtained using many different biocompatible and bioresorbable polymers, such as poly(lactic acid), polycaprolactone and poly(lactic-co-glycolic acid) copolymers, that can be wisely choose to fulfill the different medical demand. However, polyesters do not have a significant amount of functional groups on the surface and therefore a preliminary surface treatment (e.g. wet-chemical methods or non-equilibrium atmospheric pressure plasma) prior to the conjugation with biomolecules, is recommended [1]. In this work we report our last results obtained in the field of electrospun nanofibers surface bio-modification with antibodies and peptides as promising affinity membranes for cancer cell capture and exosome purification.

References:
Effect of light on biological samples deposited on different consumer relevant surfaces

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Bacteria are ubiquitous and they may cause clinical infections (e.g., in catheters or needles), corrosion, loss of efficiency in different processes (e.g., water process, bleaching teeth processes). Nowadays, many antimicrobial agents (e.g., ampicillin, ciprofloxacin) are used to avoid bacterial infections. However, when bacteria attack a surface and grow as resistant biofilms, they become less susceptible to biocides and disinfectants. Current research in the field aims to provide alternative solutions to tackle this problem, by chemical and also by physical means. An alternative solution could be the utilization of light to kill or facilitate the detachment of biofilms from different consumer relevant surfaces, whether or not in synergy with different surface modification techniques. Light treatments exhibit various advantages. They are environmentally friendly and easy to use, making them extremely desirable for the food or medical industry. They could represent a new way to tackle the biofilm problematics. The use of cheaper light sources (e.g., LED - Light Emitting Diodes) represents a future perspective for the realization of household devices or small hospital devices for photodynamic inactivation. This work aims to unravel the underlying mechanism which governs the biofilm detachment or death by investigating and optimizing different light sources.
Spectroscopic characterization of copper-based nanomaterials
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In this contribution we report on the morphological and surface chemical characterization of copper-based nanomaterials synthesized by two different routes.

Copper nanostructures were electrochemically synthesized through the sacrificial anode technique, to obtain stabilized core-shell NPs in which a metal core is surrounded by a properly selected organic shell [1, 2]. Different salts were used as stabilizers, namely tetra-butyl-ammonium-chloride (TBAC), tetra-octyl-ammonium-chloride (TOAC), tetra-dodecyl-ammonium-chloride (TDoAC) and benzalkonium chloride (BDHAC). X-ray photoelectron spectroscopy (XPS) and electronic transmission microscopy (TEM) were systematically used to study the influence of different experimental parameters on the final electrosynthesized material. Based on the results, surfactant concentration and working potential were optimized.

A second class of copper nanocomposites were obtained by modifying an already reported chemical synthesis [3]. Specifically, biocompatible chitosan flakes were added into the reaction medium in order to support and stabilize the NPs. UV-vis, TEM and XPS were performed on the nanomaterials. XPS results on the Cu-chitosan composite evidenced the presence of copper in low oxidation state, thus proving the good chemical stabilization properties of the polymeric support. Thanks to the well-known biological properties of copper, these two classes of nanomaterials have potential applications as antimicrobials.

References:
Surface characterization: a comparison between surface zeta potential techniques

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The estimation of surface zeta potential has been customarily performed by streaming potential measurements.1,2 This technique is based on the measurement of the streaming current as an electrolyte flows on the surface under analysis. In 2012, Corbett et.al.3 presented a technique for the measurement of surface zeta potential of flat surfaces based on a dip cell whereby a surface is placed between the electrodes of the cell and in contact with a tracer solution. After applying an electric field, the mobility of the tracer particles at different distances from the surface is measured using phase analysis light scattering. This data can then be related to the surface zeta potential of the sample. There is the lack of comparative literature between both techniques. Therefore, in this work I present a surface characterization study on glass and polypropylene where the two techniques are compared. Additionally, a more complete characterization of the surfaces under study is presented, including X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) measurements.

References:
Surface modified gold nanorods to provide biofunctionality
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In recent years, nanoparticles (NPs) science has progressed extensively and the application of nanosystems has become possible in a broad range of fields. Gold nanorods (AuNRs) are two-dimensional NPs characterized by tuneable optical properties which depend on their size and aspect ratio [1]. Conjugation with biomolecules make AuNRs suitable for many applications, such as bioimaging [2], photothermal therapy [3], in vivo delivery [3] and SERS-based biosensing [4]. However, the CTAB capped on the surface, derived from the synthetic process [5], limit their biological applications, since CTAB denatures biomolecules. Therefore, the discovery of new strategies to improve biocompatibility is a challenge of the utmost interest. In this work, we have used horse heart cytochrome c (Cyt c) as a protein probe to test a AuNRs system. Cyt c, a small mitochondrial heme protein, is one of the best characterized proteins due to its key role in the respiratory chain and in apoptosis [6]. Cyt c has been extensively investigated upon interaction with phospholipids in solution [7], on liposomes [8] and upon immobilization on appropriate SAM-covered electrodes [9]. However, retention of the Cyt c native structure on metal NPs has been achieved only upon conjugation to AuNPs decorated with aggregated Ag nanospheres [10]. Herein, CTAB-capped AuNRs have been coated with a negatively charged polyelectrolyte, polyacrylic acid, and then decorated with the positively charged Cyt c (due to Lys residues) through electrostatic adsorption. This system has been characterized by UV-vis absorption, FTIR and resonance Raman (RR) spectroscopies. The RR spectra obtained with both 406.7 and 514.5 nm excitation are characterized by the coexistence of oxidized and reduced Cyt c species. Nevertheless, the native structure of the protein is fully preserved.

References: