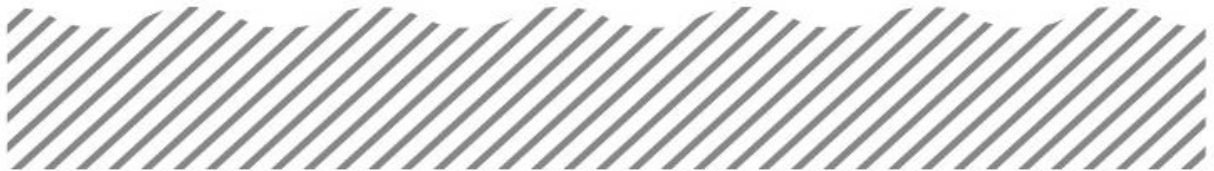


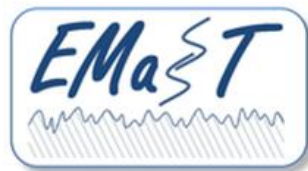


EUROPEAN SYMPOSIUM ON
Surface Science



2nd Edition

Organized by



European Association of Material
Surfaces Science & Technology

BOOK OF ABSTRACTS

Topics

SMART COATINGS & SURFACE TREATMENTS
SURFACE CHARACTERIZATION
NANOTECHNOLOGY & NANOMATERIALS

21-23 September 2016, Capri, ITALY

Welcome Message

On behalf of the Steering Committee, it is my pleasure to welcome you to the **European Symposium on Surface Science – 2nd Edition**. The Symposium provides a comprehensive overview of the state of the art in surface physics, chemistry, engineer as well as nanomaterials and in general material science, focusing on exclusive aspect related to the recent advances and current challenges, while pointing out the prospective interdisciplinary development in these fields.

The European Symposium on Surface Science represents the scheduled biannual congress organized by EMASST (European Association of Materials Surfaces Science & Technology) www.emasst.com .

EMASST was founded January of 2013 since until then there were not within Europe, Associations on Materials Science focused in particular on Surface Science. The aim of EMASST is to create and develop a cross collaboration between the research world (Universities and Research Centers) and Industrial world. In fact as our members known, EMASST promotes the international collaborations of Universities, Research Centers and Industries of EU member countries to carry out **basic research activities, industrial development, production and addition of the new products within the market** .

EMASST has the objective of creating a **"network"** on the Science and Technology of Material Surfaces among the different organizations that contribute work on these themes.

The **main purpose of EMASST** is to form a "critical mass" of people and skills on this frontier sector in order to increase and spread knowledge on the Science and Technology of the Material Surfaces at European level. In addition **EMASST spreads knowledge** and recent advances developed by its members as well as all european researchers that are working on the topics of the Surface Science. For this reason and in this frame, EMASST promote the dissemination of this new branch of Materials Science through the European Symposium on Surface Science.

Also in this second Edition of the Symposium, I was amazed of the interest showed by the people registered to the Symposium, coming from Europe: In fact I have notice a great presence of researchers coming from all part of Europe, for example: Germany, Italy, France, Greece, Poland, Austria as well as from non-european countries: Israel, Russia, Turkey.

There are many people that deserve credit for the organization of **European Symposium on Surface Science** such as the permanent Technical Scientific Committee of EMASST, the Steering Committee of the Symposium, the Organization Committee with special thanks to Dr. Dimitris Kotzias. His experience and professionalism made possible to organize The Symposium with the highest quality.

In particular I would to thanks Dr Giulia Galderisi (coordinator of the Steering Committee) for her effort and support and for her great contribution in the realization of this event.

Last but not least all of you, the participants, without which this event could not be realized.

I once again welcome all of you to the **European Symposium on Surface Science** in Capri island. I wish you an extremely fruitful meeting and a pleasant stay in Italy.

Luca MAZZOLA, August 31, 2016

President of EMASST

REACH Regulation's Impact on the Aerospace Industry.

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Since its approval in 2006 regulation 1907/2006 (REACH Regulation) was bound to have a far reaching effect on the way European Union member manage their relationship with hundreds of thousands chemical compounds present in its market.

REACH regulation have an important impact on many different industries and in their relevant markets. However, the aim of this presentation is to discuss in some depth the impact of such a regulation on the aerospace industry and more precisely the effects that REACH will have on the way both OEMs and coating producers are going to approach the important subject of corrosion prevention on aircraft's parts in a future where chromates will not be allowed anymore.

The presentation will:

- Sketch briefly the main characteristics of the REACH regulation, the rationale behind it and the main operating mechanisms;
- Analyze possible scenarios for the European and international aerospace industry supply chain and the approaches hitherto taken by the most important OEMs;
- Discuss the impact of REACH on the different aerospace market segments;
- Highlight the most updated chrome free technologies and their field of application;
- Underline the most important technological challenges in the development of new CF technology for structural application;
- Evaluate the short-medium terms activities of the different stakeholders which will characterize the way to the sunset date of 2019 for strontium chromates and other Cr6 compounds.

Improvement of service life of advanced thermal barrier coatings by nanostructuring and architecture modification

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Thermal barrier coatings (TBCs) are heat resistant and protective layers used in hot section components of gas turbine engines. A conventional thermal barrier coating system consists of a thermal sprayed Ni/Co-CrAlY bond coat, providing the oxidation and hot corrosion resistance to the underlying superalloy, and a porous yttria stabilized zirconia (YSZ) top coat (either plasma sprayed or deposited by EB-PVD) acting as an insulating layer.

On-service durability of TBCs mainly depends on porosity, compliance, toughness and thermal properties of the ceramic top coat and on the ability of the bond coat to produce an efficient oxygen barrier through the formation of a consistent alumina layer (thermally grown oxide, TGO) at the interface with the top coat.

Different approaches to the optimization of the mentioned properties are proposed: i) the use of nanostructured YSZ top coats (for increased high temperature mechanical properties and improved sintering resistance); ii) the deposition of a thin Al₂O₃-PVD sputtered overlay on the bond coat prior to top coating with YSZ (for decreased aluminum depletion of the Ni/Co-CrAlY coating and reduced thermal oxide growth stresses development).

The results of experimental investigations were analyzed considering both the microstructural features (microstructure evolution, oxide growth rates) and the engineering properties (high temperature mechanical behavior, thermal shock resistance); moreover a thermo-mechanical finite element model was developed implementing the oxidation kinetics in order to estimate the effects of the PVD film on the mechanical stress field of the TBC system.

Supercritical Fluid Deposition of silanes on solid surface for biosensing and heterogeneous catalysis applications

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Above 73.8 bar and 31.1 °C, carbon dioxide becomes supercritical and acquires remarkable properties: density close to solvents, zero surface tension, low viscosity and high diffusivity. Considered as a green solvent, scCO₂ is a promising alternative to noxious organic solvents and chlorofluorocarbons. Indeed scCO₂ is a good solvent for many non-polar (and some polar) compounds. It easily diffuses into porous materials and micro- and nano-structured devices. In this study, we have demonstrated the deposition of diverse functional organosilanes such as fluorinated silanes, aminosilanes, aldehyde silanes, mercaptosilanes and, for the first time, the 3,4-epoxybutyltrimethoxysilane (EBTMOS) on silicon oxide using a prototype of supercritical fluid deposition (SFD) equipment. (Figure 1) This equipment allows the simultaneous treatment of two 8-inch silicon wafers and offers the possibility to work with dynamic or static conditions. It is compatible with fragile structures such as micropillars silicon chips and allows to work with automated processes.

The ability of this specific EBTMOS layer to react with amine functions has been evaluated using the immobilization of amino-modified oligonucleotide probes (Figure 1). The presence of the probes is revealed by fluorescence using the hybridization with a fluorescent target oligonucleotide. The performances of SFD of EBTMOS has been optimized and then compared with the liquid phase and molecular vapor deposition methods. We have evidencing a better grafting efficiency and homogeneity and a lower reaction time in addition to the eco-friendly properties of the scCO₂. Coating has been characterized by Surface Enhanced Ellipsometric Contrast optical technique, AFM and MIR-IR. This EBTMOS based coating layer has been successfully used for the grafting of iron based, inorganic catalysts on MCM-41 mesoporous silica (Figure 1). A good catalytic activity of the supported catalyst in the oxidation of thioanisole with hydrogen peroxide was observed. These preliminary results show an enhanced catalytic activity of the heterogeneous catalyst compared to the homogeneous one.

In conclusion, this study describes some examples for the deposition of organic silanes using a supercritical fluid deposition equipment (SFD-200) demonstrating the feasibility to industrialize these SFD process of silanes for MEMS or NEMS fabrication for example.

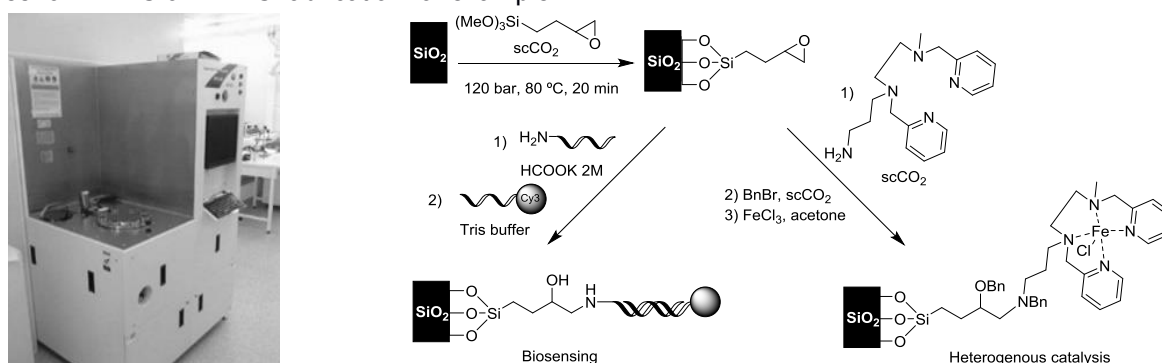


Figure 1: Photograph of the SFD-200 equipment (left). Schematic representation of silanization and grafting of oligonucleotide or iron-based catalyst (right).

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Sol–gel routes in different media to obtain nanostructured, superhydrophobic coatings on copper surfaces

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Copper is a metal with exceptional properties (thermal and electrical conductivity, alloyability, malleability, etc.) which make it the chosen material in a wide range of applications, e.g. energy conversion, heating/cooling devices, electronics. In many cases, copper is in contact with water, therefore the control of copper surface wetting can be crucial to enhance efficiency in such devices. We chose to coat copper surfaces with a hybrid, nanostructured coating in order to obtain the maximum repellence against water, e.g. superhydrophobicity. The inorganic component of the coating consisted of alumina nanoparticles, which in turn formed a nanostructured thin layer with a peculiar flower-like morphology after treatment in boiling water. We explored two sol-gel routes for the synthesis of alumina nanoparticles, namely one in water and one in isopropanol. The latter proved more efficient in forming a continuous nanostructured coating on copper surfaces, probably due to the lower surface tension and lower contact angle of the alcohol-based sol on bare copper surfaces. Eventually, only the coating obtained from the isopropanol-based route provided superhydrophobic properties after chemical modification with fluoroalkylsilane moieties. AES and XPS spectra confirmed the higher surface coverage provided by the alcohol-based sol.

Furthermore, we assessed the effect of thermal treatment temperature on surface morphology. After deposition of the alumina nanoparticles, the surfaces were heat-treated at either 200, 300 or 400°C. SEM images showed that at T 300°C the flower-like alumina was present on the majority of the surface. Rising T to 400°C caused the growth of CuO microwires that displaced the alumina coating (Figure 1). In terms of wetting behavior, also the 400°C-treated surface displayed good superhydrophobicity, but its remarkable brittleness was an important drawback. In contrast, the sample treated at 200°C could perfectly withstand ultrasonic treatment with no loss in superhydrophobicity, hence proving excellent durability.

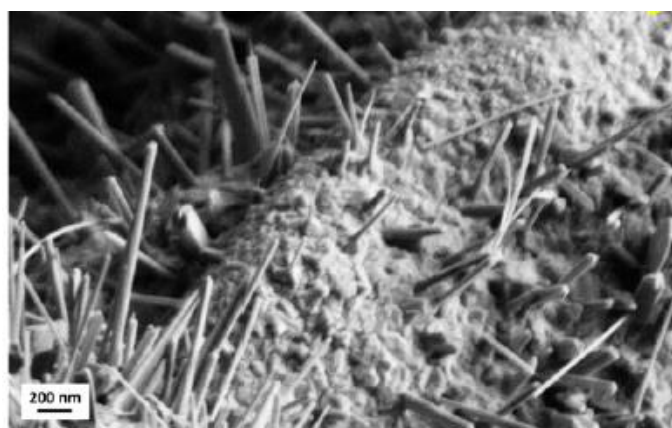


Figure 1: CuO microwires grown on a copper surface after heat-treatment at 400°C. The flower-like alumina coating was totally displaced by microwires in the investigated area.

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Passive anti-icing systems: icephobic coating for aeronautical applications

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The ice formation on a critical components such as wings and vertical tails is the main problem for the reliability and safety for aircraft flights. Passive anti-icing protections such as superhydrophobic and icephobic coatings, are potentially employed to prevent the ice adhesion and its growth.

Actually to obtain icephobic aircraft surfaces, it is necessary to apply a coating (permanent or not) that cover and mask the livery coating in contrast with the aesthetical properties of the aircraft.

The aim of this work is to develop an icephobic coating with the same aesthetical properties to the classical commercial coating used as a livery. Starting from a commercial livery coating, a new formulation was developed combining both icephobic and aesthetical properties.

In this work will be described the progress in aesthetical anti-icing coating development, starting from the basic theories of the adhesion phenomena between supercooled water droplets and surfaces (TRL1) to the design and testing of the new multifunctional aeronautical coating in relevant environment (TRL5).

In fact the best formulation and architecture of the coating system was characterized at lab scale in order to evaluate icephobic properties using a new tool mounted on classical contact angle measurement apparatus that allows reproducing the flight condition of pressure and temperature values in which there is the highest risk of icing.

Electron Scanning Microscopy and confocal profilometry were applied in order to characterize the surface morphology of the new multifunctional coating. Nanoindentation, cutting and tape test and pull-off test were carried out to evaluate the mechanical properties of coating. Moreover, the coating was treated with Skydrol in order to test its resistance to a common aviation hydraulic fluid.

Finally, a successful validation of icephobic properties of the new multifunctional coating was achieved testing it in a Icing Wind Tunnel. In fact two NACA 00015 airfoils were design and realized in ABS using Additive Layer Manufacturing and subsequently they were coated with the classical aeronautical coating and with the new multifunctional coating.

Results show a drastic reduction of the ice growth on surfaces covered with the new multifunctional coating respect to the commercial one.

Empirical Investigation on the Icing Behavior of Grid Structures in a Lab-scale Icing Wind Tunnel

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Icing represents a major problem in the aviation industry. While icing of common components such as airfoils due to the impingement of (supercooled) liquid water droplets is widely studied, even if not yet fully understood, supporting structures like grids on engine air intakes have been investigated to a lesser extent. An optimization of these protection grids will lead to reduce icing severity and, subsequently, to avoid loss of efficiency and safety issues that can lead to hazardous situations.

The presented study investigates the icing behavior of steel and nylon grids in use on helicopters. Additionally, different surface treatments are proposed to improve the passive icing protection properties of steel and nylon. The experimental work is carried out in the lab-sized icing wind tunnel iCORE (Icing and Contamination Research Facility). A variation of the most relevant parameters air stream velocity, air temperature, liquid water content of the cloud and relative humidity will allowed identifying their influence on the icing behavior of the grids (Figure 1).

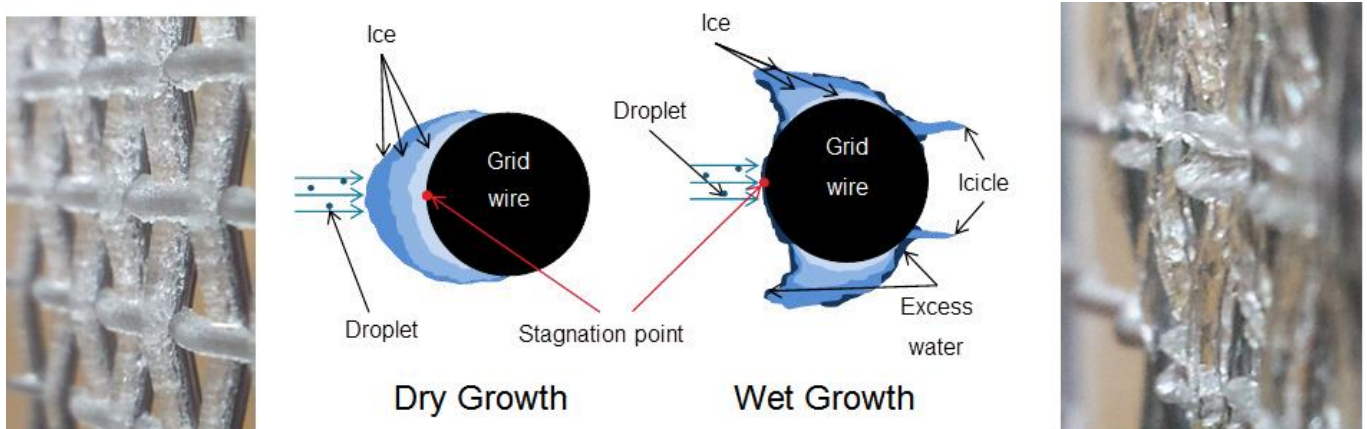


Figure 1. Schematically icing of a grid wire in dry growth (left) and wet growth (right) regime. Sequence of icing displayed by different blue tones.

After comparing the different icing behaviors of steel and nylon grids, the best configuration could be selected and proposals for further improving the anti-icing performance of air intake protection grids will be made.

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Comprehensive Wetting Analysis of Functional Surfaces

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Functional surfaces with specific wetting behavior have gained continuously increasing attention. For instance, oleophilic surfaces can optimize the lubrication of tribological systems or optical components made of surfaces with adjustable hydrophobic wetting behavior all the way to superhydrophobicity and self-cleaning can minimize the utilization of chemicals [1]. Suitable evaluation and comparison of the wetting properties require characterization methods that are well defined and focused on the particular application.

For a first assessment of the wetting properties of different solid surfaces, basic contact angle measurement parameters such as a simple apparent contact angle (CA) of a sessile drop are often used. Nevertheless, this kind of simplicity leads to a great variation in the performance and evaluation of the CA behavior depending on the specific analysis conditions: It is rather difficult to compare wetting properties resulting from different wetting analysis methods. Furthermore, in case of real surfaces, roughness and chemically heterogeneities lead to a wide range of metastable apparent CA [2]. For example, our systematical investigations of a large variety of surfaces revealed the absolute necessity of determining the advancing CA and receding CA for a complete characterization of hydrophobic surfaces [3].

In this talk, we will describe in detail the development of advanced methods for a more thorough wetting analysis with the aim to characterize specific wetting systems (e.g. different surface materials and liquids, varying environmental conditions) as well as to classify extreme wetting properties.

Examples are given for nano-rough surfaces with adjustable wetting properties.

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Advanced Roughness Analysis of Functional Nanostructures for Optical Applications

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There is an ongoing trend of requests for surfaces that cover several different functionalities at once. Examples are combinations of extreme wetting behavior, special optical properties, and high mechanical robustness. The technical realization of such multifunctionality enables e.g. equipping optical components with self-cleaning, anti-fogging or anti-icing effects while ensuring long-term stability.

Especially the roughness structure of the surface, in addition to the chemical composition, has been shown to be responsible for such smart wetting behavior [1]. On the other hand, surface roughness, although required for the functionality, can also be a critical factor for optical applications. This is mainly because even small amounts of surface roughness give rise to light scattering causing unacceptable optical properties [2].

Essential for developing multifunctional surfaces is hence a careful control of their roughness structure, which implies a thorough characterization of the surface roughness within the entire range of relevant spatial frequencies.

In this talk, we will demonstrate how this can be achieved by combining different metrology approaches such as atomic force microscopy, white light interferometry, and light scattering. Using our specific modelling, measurement and analysis procedures based on Power Spectral Density (PSD) functions [3] we are capable of predicting, defining, and controlling roughness structures for optimal surface properties. Applying this advanced roughness analysis enables us even the separation of the influence of roughness and material properties on the wetting behavior [4].

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SAXS Investigation of Surface Fractal Dimension of MnO₂ Pyrolytic Nanocompositions

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MnO₂ films which have been prepared by the thermal deposition (pyrolysis) of Mn(NO₃)₂ are important semiconductor materials for application as semiconductor layer in metal (sintered Nb pellet) – dielectric (anodic Nb₂O₅)– semiconductor (MnO₂) MDS electrical capacitors. Earlier reported significant influence of the fractal layer on electrical characteristics of MDS capacitors. This feature are responsible for the interest in investigating the fractal properties of this latter.

The surface fractal dimension D have been investigated by small-angle X-ray scattering (SAXS). The theory of scattering by a porous solid was developed by Wong. The main formula of this theory is as follows:

$$I(q) \sim (\text{constant} \times q^{D-6}) \quad (1)$$

Here $I(q)$ is the X-ray scattering intensity, q is the wave vector, and D is the surface fractal dimension. shows the fractal behaviour. Indeed, on the graph the coefficient of the slope of the curved part, which can be closely approximated by a line, α , is:

$$\alpha = -d \ln I(q) / d \ln q = 2.87 \quad (2)$$

In case when $2 < \alpha < 3$, the scattering cause by the **whole volume** of subject and $D = \alpha = 2.87$. The obtained D value coincides with previously found value of surface fractal dimensionality in a sintered niobium powder pellet with high accuracy $D_{(Nb)} = 2,81$ (see formula (1) at $\alpha = 3.19$). So far, authors are at loss and cannot say whether it is a mere coincidence or the result of some specific features of generation of the capacitor MDS structure. But it as should be noted earlier in case when $2 < \alpha < 3$ scattering stipulate by the **surface** of sample.

Zeta potential of solid surfaces: a poorly explored, but useful and versatile tool in surface analysis of bulk samples

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Zeta potential is a widely employed technique in the field of the colloidal suspensions, especially for investigation of their stability, but it is still poorly applied to solid surfaces. As far as solid surfaces are concerned, zeta potential describes surface charging behavior in contact with the water-based media and gives information about the functional groups exposed on the surface, the interaction of the surface with the compounds dissolved in a solution and during absorption processes at the solid-liquid interface [1]. The Zeta potential measurements allowed determination of the isoelectric point of the surfaces and their surface charge in function of pH. The Zeta potential measurements are of interest for various applications involving materials surface interaction with liquid media such as membranes and filters, biomaterials, semiconductors, fibres, cosmetic and detergents, polymers and minerals.

In the present research, Zeta potential was measured by electrokinetic measurements (SurPASS, Anton Paar) on different solid surfaces. Surface zeta potential was determined in function of pH in a 0,001 M KCl electrolyte solution varying the solution pH by addition of 0,05M HCl or 0,05M NaOH through the instrument automatic titration unit. The instrument and a scheme of the measuring principle are presented in Figure 1a. In Figure 1b, Zeta potential measurements performed on different materials (metal, ceramic and polymer) are reported as an example: different isoelectric points and slope of the curves can be observed and will be discussed. The effects of several surface modification processes can be investigated by this technique. The difference between the surface charge and isoelectric point of polystyrene for cell cultures (polystyrene surface modified by the corona treatment) and polystyrene for bacterial cell culture (untreated polystyrene) is presented in Figure 1c and the difference between a polished Ti6Al4V alloy and a chemically treated (CT) one is shown in Figure 1d. Moreover, surface reactivity of various materials (e.g. titanium alloys and bioactive glasses) has been successfully monitored in Simulated body Fluid looking at their charging behavior at different time-points.

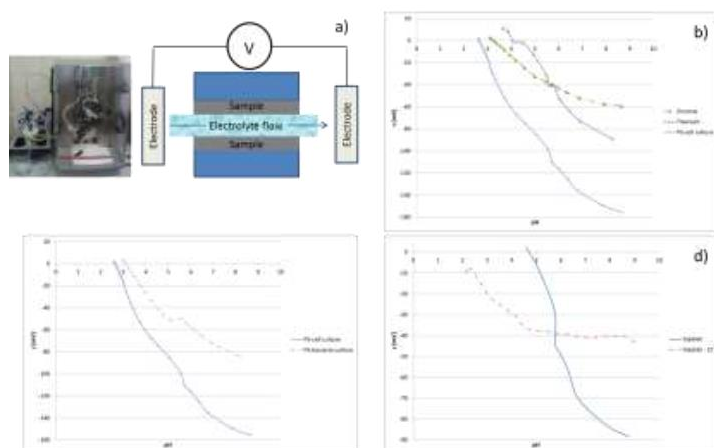


Figure 1: (a) Instrument for Zeta potential measurements and a scheme for the measuring principle, (b) measurements on different materials, (c) measurements on polystyrene with different surface treatments and (d) measurements on Ti6Al4V with different surface treatments

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IPR Management and Technology Transfer at the CNR. Procedures and best practices

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With more than 8000 employees, 4500 of which are researchers, the Italian National Research Council is the largest research institution of Italy, and the fourth larger research center in Europe. As a public funded institution CNR must comply with a number of laws and regulations intended to assure that the public owned IPR be exploited in the best interest of the community. Also the great number of researchers translate into a huge amount of invention proposals that must be accurately checked and evaluated in order to balance the scientific and technological perspective with the necessity of a rational and fair use of public funds.

In this talk the organization, structure and best practices and procedures in use at CNR are described, with a focus on the relationship with foreign partners and the different exploitation strategies used.

Titanium anodic oxidation: from surface functionalization to corrosion and environmental properties

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The reactivity of most metallic surface can be source of adverse consequences, as in the case of undesired corrosion reactions, but it can also present beneficial aspects, as the possibility to tune surface functionalities through electrochemical processes. Anodic oxidation can induce the formation on titanium of different titanium oxides with controlled features, The process parameters which most determine the properties of the growing oxide are the electrochemical ones as well as the electrolyte specifications and, of course, the composition of the metal itself and its surface conditions. Tuning the operating process parameters it is possible to obtain TiO₂ films that differ in terms of thickness, morphologies, and oxide structures.

Based on oxide characteristics, three main types of anodic oxidation processes can be identified: traditional anodizing –thin compact films showing interference colors; anodizing in fluoride containing electrolytes, causing the growth of nanotubular oxides; and high voltage anodizing, also called Anodic Spark Deposition (ASD), or Plasma Electrolytic Oxidation (PEO), or MicroArc Oxidation (MAO).

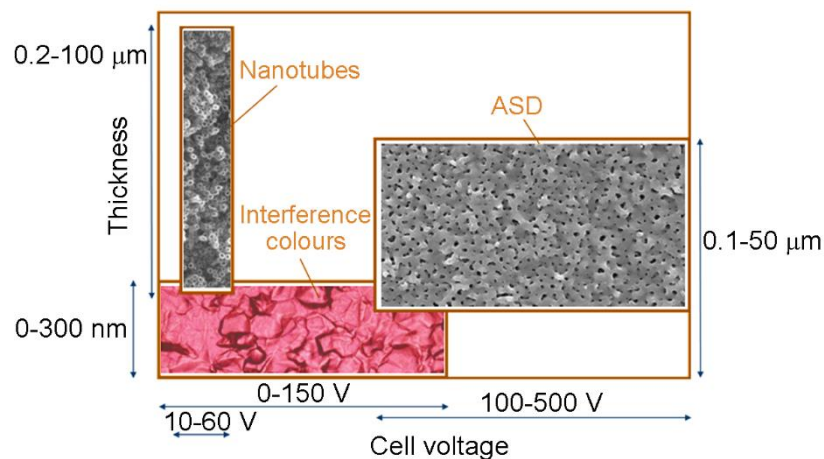


Figure 2. Map of anodizing techniques as a function of applied voltage, and related range of oxide thickness

A precise and robust control of the anodizing process is of fundamental importance in tailoring properties of anodic TiO₂ surfaces for several functional properties, as corrosion resistance, biocompatibility and photoactivated preproperties, as well as aesthetical properties. The work is aimed at providing a survey of techniques and parameters that allow to achieve controlled oxide features as a function of the desired field of application.

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Self-assembled nanoscale films and complexes of the surface active protein Vmh2

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Hydrophobins are surface active proteins endowed with adhesive properties, which play multiple roles in fungal biology.^[1] Due to their peculiar structural and physicochemical characteristics they are able to self-assemble into amphiphilic monolayers at liquid-air and liquid-solid interfaces, acting as biosurfactant and as coating respectively. Moreover Class I hydrophobins can assemble into amyloid-like structures and form remarkably stable layers which can be depolymerized by strong acids such as at 100% trifluoroacetic acid.

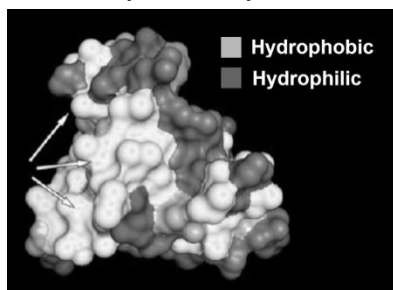


Figure 1. Model of Vmh2 hydrophobin. Arrows indicate a large hydrophobic exposed area corresponding to 27% of the total area (2117 Å² out of 7811 Å²).^[2]

The Class I hydrophobin Vmh2 extracted from the edible fungus *Pleurotus ostreatus*, is one of the most hydrophobic hydrophobins known.^[2] The self-assembled Vmh2 layer is able to change the wettability of various surfaces such as steel, silicon, glass, and gold, and to adsorb other proteins in their active form as well as nanomaterials.

Its adhesive properties have been tested in a range of applications that require the bioconjugation of nanomaterials or proteins to devices without affecting the optical properties of the materials and the biological properties of the biomolecules. The proteinaceous layer has been proven functional in microarray technology^[3] and for Matrix Assisted Laser Desorption Ionization (MALDI) mass spectrometry analysis.^[4–6] Moreover nanocomplexes of Vmh2 with nanomaterials such as graphene and gold nanoparticles have been prepared by one step approaches. These procedures led to stable dispersions of few-layer defect-free microsheets

of bio-graphene^[7] and to Vmh2-gold complexes sensitive to glucose.^[8,9]

In conclusion, this versatile protein represents a green tool for surface modification of bulk and nanosized materials, for device applications.

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Expanding the spectrum. How in-situ complementary spectroscopies can enhance surface and thin film analyses

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Advanced materials present ever increasing challenges to the analytical scientist. Composite materials built from nanostructures or ultra-thin films, often with complex chemistries present, are now required in a broad range of applications, and achieving full characterization is rarely managed using only one analysis method. To maintain confidence in the results from the utilization of several different methods, it is advantageous to be able to perform experiments on the same platform. Ideally, this should be without having to move the sample, removing the need for additional registration or processing to ensure that the data is being collected from the same position.

We have recently integrated further instrumentation onto an XPS system. The integrated system has combined a Raman spectrometer with a micro-focused, monochromated XPS system. The focal points are aligned such that data can be acquired from the same point simultaneously, and that the sizes of the analysis areas are comparable in size. This combined approach is particularly powerful when analyzing carbon nanomaterials. Chemical modifications of the material can be easily determined and quantified with XPS, and Raman offers a fast way of determining the quality and conformity of the material. The greater depth of field of the Raman spectrometer also offers bulk information to complement the surface sensitive XPS data.

In this presentation we will discuss the strengths of this combined, in-situ approach to surface analysis, illustrated with examples from a range of applications including carbon nanomaterials.

Smart surfaces: self-cleaning titanium dioxide (TiO₂) coatings for depollution purposes

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Photocatalytic oxidation is an advanced oxidation process that uses solar energy (UV light) for the degradation of environmental pollutants. Light excitation of TiO₂ semiconductors, at wavelengths between 360-380 nm, generates positive holes in the valence and electrons in the conduction band, respectively. These species are very reactive and can either recombine or diffuse to semiconductor surface where they are trapped by adsorbed molecules of water and oxygen. They initiate the formation of hydroxyl radicals and other reactive species that attack pollutant molecules and thus degrade them. For example the harmful NO_x gases are oxidized to nitrates by using UV radiation to activate the TiO₂. Laboratory and real scale data obtained within the frame of various projects indicated that TiO₂ containing paints efficiently destroy upon irradiation with UV light the ozone precursors NO and NO₂ up to 80% and 30%, respectively. The photocatalytic conversion of NO increased with the decrease of relative humidity (50%→20%) and the photocatalytic rate of NO was calculated to be between 0.11 μg m⁻²s and 0.42 μg m⁻²s, depending on the humidity level [1,2,3].

TiO₂-Photocatalytic materials and coatings when used as outer layer on buildings located in highly traffic roads have shown efficiency to degrade priority air pollutants (e.g. NO, NO₂) originated from traffic exhausts. In the last ten years, however, research was focused onto the application of smart photocatalytic materials and coatings, which could improve the quality of indoor environments too. In this context, a Mn-doped amorphous TiO₂ photocatalyst powder containing was successfully applied for the oxidation of NO under indoor-like illumination conditions. After it was added to a calcareous matrix commonly used in the formulation of building products, the photocatalyst demonstrated its ability, in this form too, to degrade upon irradiation with visible light up to 95% of NO after 6h of irradiation, without any significant photocatalyst inactivation. Results from these experiments demonstrate that, with selection of both the appropriate dopant and its concentration, the photo-assisted elimination of air pollutants is a promising technique for remediation purposes in indoor environments [4.]

The development of innovative building materials and coatings (containing TiO₂) and the development of catalysts activated by visible light are two fields of innovative research to be addressed in future investigations [3]. Moreover, targeted studies addressing the efficiency of photocatalytic materials on the degradation of chemical mixtures including the determination of eventually formed, toxicologically relevant, by-products are needed in order to evaluate the applicability of these materials and coatings indoors.

Development and application of smart photocatalytic materials in view of their potential use in indoor environments too, will be addressed and discussed.

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Smart Modification of titania for Visible Light Photocatalysts: A Mn²⁺ doping study

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Clean air is vital importance for our health. Especially in urban areas of the industrialized world, air pollution from inorganic and organic pollutants, is one of the greatest environmental challenges. The already overburdened outdoor air adds to poor indoor air quality which in selected cases might be even 12-fold more polluted due to a number of objects that emit compounds harmful for our health and body, causing from minor headaches and discomfort to serious respiratory problems. It is therefore a key factor in the overall quality of our life, to improve and maintain good air quality both outdoors and, in particular, indoors.

TiO₂ plays the most important role owing to its excellent chemical and physical properties, for a wide range of applications (such as environmental, energy etc.) and especially for air cleaning. However, the TiO₂ band edge lies in the UV region that makes them inactive under visible irradiation and suitable only for outdoor applications. In this regard, considerable efforts have been made to increase the visible light activity of TiO₂ via modification of its electronic and optical properties with doping. Doping TiO₂ using either transition metals is one of the typical approaches that has been largely applied. This work summarizes our recent research results on transition metal doped in titania. In particular, we focused on the role of Mn. Synthesis of Mn doped anatase (TiO₂) nanoparticles using titania and manganese salts as the starting materials, is very simple quick and inexpensive. The crystalline structures and morphologies of the materials have been characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Transition Electron Microscopy (TEM). The oxidation state of Mn(II) and coordination environment were determined using electron paramagnetic resonance (EPR). Photocatalytic activity of the materials were studied to the degradation of aqueous and air pollutants.

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Green, efficient graft modification of multiwalled carbon nanotubes with dye diazonium salts in water

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Diazonium surface modification has received much attention since two decades as it applies practically to all types of materials [1, 2]. This surface chemistry has many appealing features: operation at room temperature, in aqueous or organic solvents and without necessarily the use of a reducing agent if the substrate has sufficient reducing power; more importantly it gives true covalent bonds between the substrate and the aryl group resulting from the reduction of the diazonium salt. Herein, we concentrate on tuning the surface chemical composition of MWCNTs using diazotized dyes in a green and efficient manner. Indeed, reductive grafting was achieved in water at RT without any reducing agent, an option that has not been explored so far. Moreover, both the nature and the initial concentration of the diazotized dyes were changed.

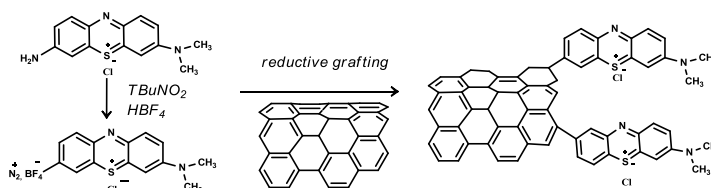


Figure 1. General pathway to dye-functionalization of CNTs with diazotized dye and spontaneous aryl grafting to MWCNTs. Example is given for Azure A diazonium.

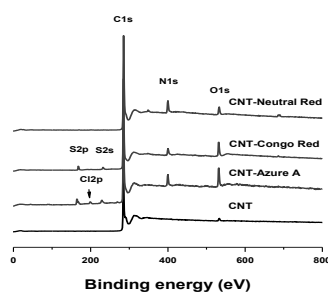


Figure 2. XPS survey regions of pristine and dye-modified CNTs.

The as-modified MWCNTs were examined by IR, Raman, XPS, TGA and TEM. XPS brought strong supporting evidence for the modification of the surface and particularly for the loss of the F1s from BF_4^- anion together with a clear change in the high resolution C1s region from the modified nanotubes.

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Transport Properties of Intrinsic and Dirty Graphene with EMC: The Role of Various Scattering Mechanisms

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The electronic transport properties of intrinsic and dirty graphene sheets are studied with an Ensemble Monte Carlo (EMC) technique. The relevant scattering mechanisms that are taken into account for both cases are nonpolar optic phonon and acoustic phonon, ionized impurity, interface roughness and surface polar phonon scatterings. SiO₂ is used as a substrate in this study because the effect of surface polar optic phonon scattering is minimal for SiO₂. The effect of screening is considered both in the ionized impurity and surface polar phonon scatterings of electrons. The scattering rates were calculated using Fermi's golden rule. A rejection technique is used in EMC simulations to account for the occupancy of the final states. The variation of electron mobility as a function of electron concentration is investigated in the presence of various scattering mechanisms including surface polar phonons for dirty case. The mobility values for dirty graphene as a function of electron concentration are compared with the experimental mobility results at different temperatures.

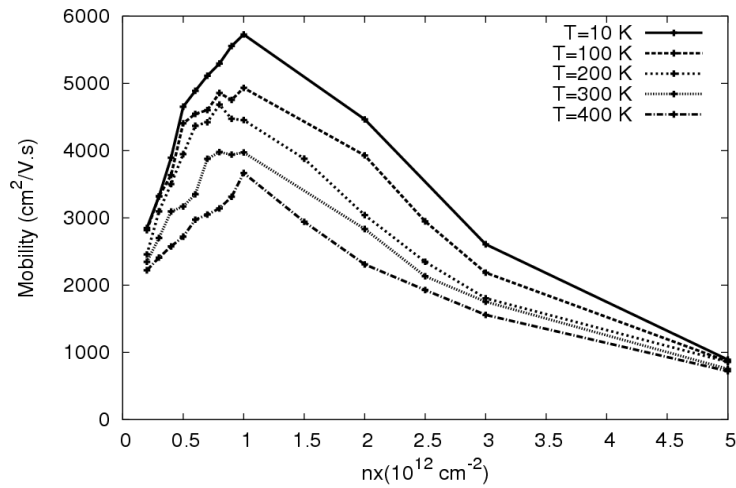


Fig. 1 The change of mobility with electron concentration, in the presence of all scattering mechanisms (dirty graphene case)

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Innovative self-cleaning membrane preparation for water treatment applications

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A novel self-cleaning strategy against the irreversible fouling of porous membranes is presented. In particular, the catalytic H₂O₂ dismutation, into water and oxygen, was exploited as a novel antifouling approach. To this aim, the tetra-ruthenium substituted polyoxometalates (Ru₄(SiW₁₀)₂) (Ru-POM) were integrated into the polymeric membranes [1]. The in-pore O₂ evolution, resulting from H₂O₂ dismutation mediated by the Ru-POM, represented the propulsion force for the displacement of foulant particles located on the pore mouth and in the inner pore walls of the membrane.

Porous polymeric membranes of polyether ether ketone with “cardo” group (PEEK-WC) embedded with Ru-POM nanoparticles were produced by phase inversion technique, under controlled humidity and temperature. The self-cleaning properties of the membranes were established by monitoring the removal of polystyrene solid latex beads (used as model fouling agents and deposited at membrane surface) by confocal fluorescence microscopy, applying aqueous H₂O₂ (2M) which acted as a chemical trigger for through-pore oxygen evolution. The O₂ propulsion force was strong enough to enable the rejection of the model foulant particles from the pores liberating the membrane from the fouling. The oxygenic evolution at the membrane surface by using POM complexes represents, therefore, an innovative method for reducing fouling formation from the membrane (membrane self-cleaning) guaranteeing a long-term efficiency of the material.

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