FUNCTIONAL NANOSTRUCTURED AND MOLECULAR SYSTEMS

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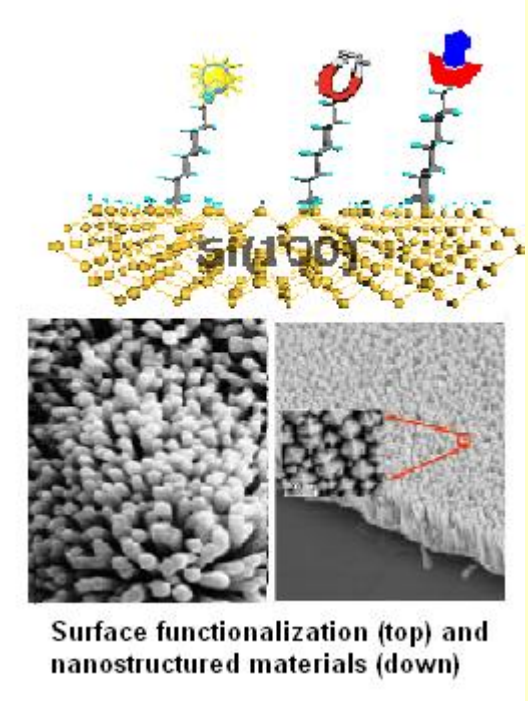

Surface functionalization (top) and nanostructured materials (down)

The quest for future technologies is focused on the development of new smart materials permitting to improve the present technology by enhancing the efficiency of the operations, by allowing the miniaturization of the devices and permitting the introduction of innovative concepts. In our activity, we want to pivot our research on nanostructured and hybrid organic and inorganic systems. The research is focused on the development of bottom up techniques for building hybrid nanostructures. The goal is the assembling of new structures with tailored magnetic, optic and electric properties coming from both the nature and the size of building blocks, and often more interesting than bulk materials. The combination of molecular systems with inorganic substrates allows the design of materials with various functionalities as molecular recognition, specific optical and magnetic properties.

Keywords: oxides, thin films, surface functionalization, bottom-up, DFT modelling

1. Synthesis of nanostructured thin film

The interest in nanoscale materials stems from the fact that new properties are acquired at this length scale and, equally important, that these properties change with their size or shape. The development of new synthetic methods has made it possible to produce uniform nanostructures with sizes ranging from 1 to 100 nm and with new shapes (rods, wires, cubes, spheres).

1.1 MOCVD processes: a bottom-up approach from molecules to functional nanosystems

Involved Researchers: Graziella Malandrino, Maria Rita Catalano

The bottom-up strategy represents the most used route to prepare nanostructures, and in this perspective, the metal organic chemical vapor deposition (MOCVD) processes may be envisaged

as a natural bottom-up approach starting from molecule, commonly known as precursors, towards the formation of nanosystems. This synthetic approach has proven suitable for the fabrication of nanosystems going from the simplest in chemical nature such as metals to the most complex multi-component oxides. Binary oxides of lanthanides and transition metals have been fabricated in form of ultra-thin layers (Pr_2O_3 as high-k dielectrics and NiO, a p-type semiconductor with antiferromagnetic behaviour) and nanotube arrays (NiO, Co_3O_4). Nanoscaled materials with a complex perovskite based structure show great potentialities in a wide variety of applications and in several technological fields, including optics, microelectronics and catalysis. Chemical vapor deposition processes have been shown to be well suited also to this aim. Various perovskite based nanostructured films have been fabricated going from the superconducting $La_{2-x}(Ba)_xCuO_4$ to the giant k $CaCu_3Ti_4O_{12}$ from the host matrices $LaAlO_3$ and $YAlO_3$ to the magnetoresistant $La(Sr)MnO_3$.

In summary, the possibility to tailor the nanostructure, either using processing parameters or template systems, makes MOCVD a very promising route to the formation of nanostructures of simple and complex chemical nature.

1.2 Multifunctional ZnO Nanostructures

Involved researchers: Maria Elena Fragalà, Iana Aleeva

Metal oxide nanostructures, characterised by multiple morphologies and structures are at the forefront of application driven nanotechnology research. In particular, they represent a versatile solution for performance enhancement and applications in multifunctional devices and offer distinct advantages over their bulk counterparts The present research activity is mainly dedicated to fabrication and surface functionalization of ZnO nanostructures using different synthetic approaches ranging from vapour phase deposition (MOCVD) to solution growth (Chemical Bath Deposition).

Hybrid synthetic approaches are used to obtain ZnO nanostructures having dual or multiple morphologies. The further functionalization of these inorganic structure, using non covalent and covalent grafting of organic molecules having specific chemical behaviour offers interesting potentiality for the design of high performance devices. Hierarchical ZnO nanostructures growth on TiO2 nanofibers have been obtained by combination of electrospinning with MOCVD or CBD. Moreover, integration of MOCVD and CBD with colloidal lithography (CL) has proven effective to define 2-D hybrid ZnO-SiO2 nanoarrays having great potential as innovative fluorescence sensing substrates, with individual addressability and tuning of the biomolecular detection capability

2. Molecular engineering on inorganic surfaces

The introduction of specific functions onto inorganic surfaces represents one of the major themes in contemporary chemistry because of the potential applications in the fabrication of advanced materials performing specific functions such as memory storage elements, molecular switches, sensing devices.

2.1 Molecular engineering of silicon and nanostructured metal oxides

Involved researchers: Guglielmo Guido Condorelli, Cristina Tudisco, Emanuele Smecca, Alessandro Motta

Among various inorganic materials, two different classes of inorganic platform are particularly interesting: silicon and functional metal oxides. Silicon is a particularly attractive inorganic surface, as Si-C bonds allow for the construction of robust and durable devices by forming stable Si-**C** covalent bonds. One of the key points in the fabrication of these molecular functionalized surfaces is that the molecular properties should be transferred intact to the inorganic surface. In the chemical sensing, a first effort in this direction has been performed in our group, focusing on the grafting of tetraphosphonate (T_{iiii}) and quinoxaline (QxCav) bridged cavitands. Silicon surfaces grafted with T_{iiii} and QxCav can detect, respectively, methyl-ammonium guests from solution and aromatic VOC from gas phase. As regards the nanoassembly of 3D structures on the silicon surface, we developed a two-step strategy to assembly cavitand-based coordination cages (CSA) on Si. On the other hand, Si-grafting routes of inorganic complexes are also of interest to impart specific optical and magnetic properties to the surfaces. In this context, multy-step synthetic procedures, based on reactions performed directly on monolayers allowed the silicon anchoring of inorganic complexes not suited for direct hydrosilylation, as single molecular magnets (SMMs) or luminescent diketonate complexes . As regards functionalization of nanostructured oxides, some anchoring

strategies based on carboxylic or phosphonic tethering groups have been studied, to fabricate multifunctional systems in which molecular properties of the anchored molecules are added to properties of the oxides.

2.2 Molecular engineering on dielectric and conducting transparent oxides

Involved Researchers: Antonino Gulino, Fabio Lupo, Andrea Cristaldi

The research activity is focused on the synthesis of hybrid materials based on molecular monolayers hosted on technological substrate SiO_2 and other metal oxides suited for application in integrated devices. Therefore, the research points first on surface funtionalization processes. A fundamental issue for this purposes is the control of the grafted molecule arrangement on the surface. The overall research activity deals with synthesis, characterization and grafting of new molecular building blocks (i.e., porphyrins, metal polypyridyl complexes) for photonic, magnetic and for data storage applications. The monolayer structure are resolved by XPS and synchrotron X-Ray Reflectivity (XRR) measurements. Optical tests of monolayer-based hardware are also performed by luminescence and UV-vis measurements and monolayers are screened against various organic and inorganic chemical inputs. In particular, this study involves the chemical modulation of the redox properties of some Ru, Os, Rh and Co metal complexes by chemical analytes. Competition experiments, solvent and matrix effects are also probed. Therefore, the monolayer response is based on optical intensity monitoring (output). With this approach, we achieve stable, reproducible responses upon repeated exposure. Other systems as porphyrins behave as redox-active molecules, whose redox potentials can be tuned through synthetic design. Moreover, when attached to an electroactive surface, information can be stored in the discrete redox states of the molecules. Therefore, some appropriate porphyrin molecules have been assembled on SiO_2 and for comparison also on Si(100) surfaces and are currently under investigation.

3. DFT modeling of catalytic reactions

Involved Researchers: Ignazio Luciano Fragalà, Alessandro Motta

"Theoretical characterization" plays an important role both as a parallel instrument for analysis, and as a predictor. In this context, the attention has been focused on theoretical aspects involved in the propagation step mechanism of catalytic processes using Density Functional Theory methods (*DFT*). In particular, the stereochemical aspects of olefin polymerization processes mediated by the "Constrained Geometry Catalyst"$(CGC)^+$ has been investigated. The role of the cocatalyst was analyzed with regard to understanding kinetic, mechanistic, and energetic aspects of ethylene insertion. The energetics of catalyst activation are analyzed and compared to experiments. The energetics of heterolytic ion pair separation are scrutinized, and the effects of solvent environments assessed. Similar calculations have been carried out for the distinctive center-to-center cooperative catalytic properties exhibited by bimetallic CGC. In this case the aim was to analyze metal-metal proximity effects on ethylene polymerization processes mediated by bimetallic catalysts. An important recent development in my theoretical activity regards the application of computational method to periodic systems. In this context, the attention has been focused on the catalytic properties of the organozirconium precatalyst $Cp_2Zr(CH_3)_2$ chemisorbed on dehydroxylated γ-alumina (Al_2O_3). The interaction between the catalyst species and the surface was scrutinized and the ethylene insertion process on the surface was modeled.

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Selected Publications

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