Interdisciplinary Center for Advanced Science and Technology (ICAST) at the University of Split

ICAST is an interdisciplinary initiative in nanoscience, including nanobiology, structured optical and catalytical materials for biosensing, fuel and solar cells. Research projects at ICAST are based on multi-disciplinary approach to the scientific topics that unifies advanced computer simulations, which are the expertise of the ICAST scientific team, with the experiments at the scientific frontiers that are realized through the cooperation with a number of Universities in Europe and in the US. Director of ICAST, Prof. Dr.Dr.h.c. Vlasta Bonačić-Koutecký is an internationally recognised scientist in the fields of theoretical chemistry, nanocluster physics, photochemistry and femtochemistry.

Metal nanoclusters are building blocks in nanostructured materials. The size scale of such nanosystems corresponds to the size of functional proteins. Therefore, the formation of hybrids between nanostructured materials and proteins opens new fascinating possibilities for the creation of functional materials with novel and superior catalytic, optical and biorecognition properties. Moreover, nanoclusters are recognized as catalytic centers and are thus higly important for industrial catalysis. One of the main research fields at ICAST is an improvement of catalysits using the selective characteristics of nanoclusters for higher efficiency of fuel cells and their use in transport. Finally, the development of new materials for solar cells is based on preparation and characterisation of new metalo-organic compounds capable of transformation of photons into energy.

Research directions at ICAST:

1. Development of new generation of nanostructured biosensing materials

The goal of this project is to develop a new generation of hybrid nanostructured materials for labelfree biochips that will significantly improve the performance of microarray technology and sensitivity of the presently used microarrays for bioanalytic applications and especially for medical molecular diagnostics.
Our objective in this project is to exploit the unique optical properties of small size-selected noble metal clusters supported on surfaces and linked to proteins (antibodies used in medical applications) for development of new nanostructured hybrid materials for label-free optical biochips. For this purpose, the absorption, photoemission and energy transfer processes in metal nanocluster-protein hybrids will be optimized by the advanced multiscale modelling of their ultrafast dynamics and optical response. The goal of the theory is both to control the ultrafast light induced processes which govern the optical response and functionality of these materials and to optimize fundamental parameters of the hybrid materials such as the structure and size, fluorescence quantum yield, and ultimately label free detection signal. Furthermore, we will explore the possibility of increasing the sensitivity and reproducibility of biochips beyond current capabilities by using optimal quantum control with advanced shaped light sources. In this way, a completely new dimension will be added to the current optical sensing techniques extending their limit of detection (sensitivity) and improving reproducibility. Our collaborative project will unite advanced theoretical modelling by the groups at ICAST and the Free University in Berlin with fundamental experimental studies in the gas phase (Univeristy Claude Bernard Lyon 1), in solution (University of Geneva) and at surfaces (University of Birmingham) as well as with industrial production of biosensing materials and their medical diagnostic applications via Inanovate UK Ltd. (INA).

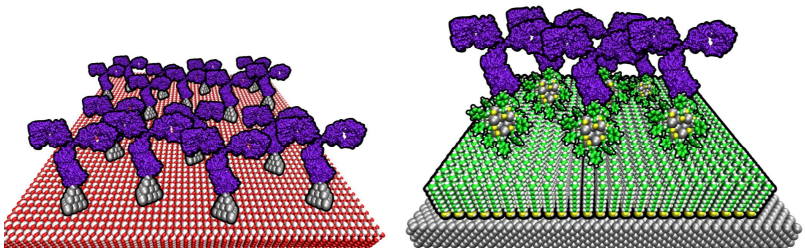

Figure 1. Artistic view of the new hybrid nanostructured materials composed of metal nanoclusters pinned at surfaces to which proteins are bound.

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2. Metal clusters for optical detection of biological aging

The fluorescent markers are a commonly used technique for detection of protein carbonylation, which is a measure of biological aging. For this purpose organic chromophores such as DNPH have been standardly used. In this project we propose to significantly increase the performance of such markers by exploiting metal clusters enhanced absorption and fluorescence. Such an enhancement effect is required in order to enable in vivo detection of the carbonylation. The advantage of using metal clusters is that they are biocompatible, soluble, robust in terms of optical properties and small enough to pass through the cell membranes in contrast to quantum dots. Therefore, small clusters in combination with optical markers such as DNPH are excellent candidates for quantification of carbonylation sites. The development of such hybrid markers will be guided by joint theoretical and experimental studies. The localization of carbonylation sites will be used in combination with molecular genetics to incorporate a Fluorescence Resonance Energy Transfer (FRET) system close to the carbonylation site and therefore detect energy transfer between the donor and small silver clusters bound to the carbonylation site. The theoretical modelling will be used to design suitable FRET donor-acceptor systems and to predict novel optical properties due to functionalization of clusters.

International Laboratory for Nano Clusters and Biological Aging, LIA NCBA (2011-2015) has been approved by the Centre National de la Recherche Scientifique (CNRS) and University of Lyon in France. Partners in this project are University Claude Bernard Lyon 1 from France, Mediterranean Institute for Life Sciences (MedILS) and ICAST at University of Split.

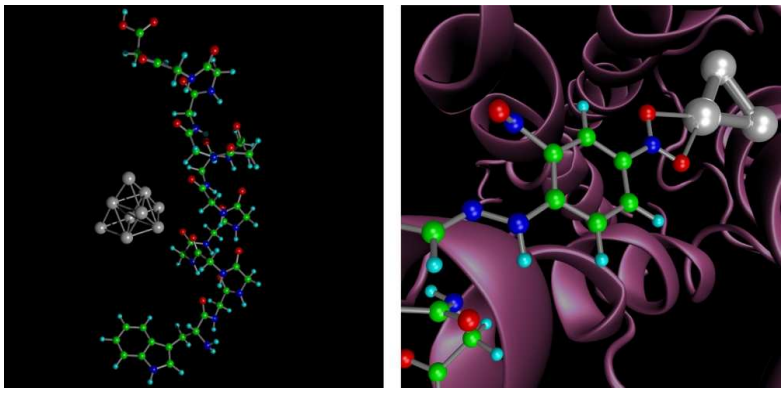

Figure 2. Left: Fundamentals for sensing by small metal clusters. Right: Probing protein carbonylation in the context of biological aging.

Relevant publications:

1. R. Antoine, F. Bertorelle, M. Broyer, I. Compagnon, P. Dugourd, A. Kulesza, R. Mitrić, V. Bonačić-Koutecký: "Gas-phase synthesis and intense visible absorption of tryptophan-gold cations", *Angew. Chem. Int. Ed.*,48,7829 (2009).
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3. Development of new materials for solar cells

We propose to prepare, characterize and investigate porphene the first heterocyclic analog of graphene, derived from porphyrin in the same way in which graphene can be derived from benzene. At present, graphene is the only known fully conjugated two-dimensional polymer. It has remarkable properties such as high electrical conductivity and mechanical strength, and it promises numerous applications, e.g. in nanoelectronics, nanooptics, biology, energy storage and solar cells. In many of these applications, graphene needs to be functionalized to prevent excessive aggregation through pi-stacking. It is unfortunate that chemical functionalization strongly perturbs the electronic structure of graphene by taking sites out of conjugation and destroying the local symmetry. In contrast, porphene will have a fourfold instead of a six-fold symmetry and its electronic structure and properties will differ from those of graphene. It will also differ from graphene in that it will be easily functionalized without taking any sites out of conjugation, because a metal ion can be inserted into the center of each porphyrin ring. Moreover, a fifth or even a sixth ligand can be attached to the metal. Since one can choose among dozens of possible of closed-shell or magnetic metal ions and hundreds or thousands of electroneutral or charged ligands, there will be ample opportunities to tune the properties of porphene. It is also easy to imagine how multiple layers of porphene could be constructed in a well-defined fashion through the use of rigid bifunctional ligands. Our joint theoretical and experimental investigation will include basics and applications. One can anticipate that the choice of ligand will provide control over the position and shapes of electronic structure bands and thus over electronic conduction, optical properties such as the bandgap, magnetic properties, etc. It is likely that the most valuable properties of such entirely new and unexplored materials will be those that we have not even thought of. An example of possible application that can be envisaged readily is to prepare a porphene sheet carrying electron donors on one side and acceptors on the other, and to use the spectral properties of the ligands or of porphene itself for the capture of solar photons and their conversion into spatially separated electron-hole pairs. Since the electrons would all be on one side and holes all on the other side of the porphene sheet, the structure would resemble a well-defined p-n junction. Electrodes, possibly represented by additional parallel porphene sheets if they are conductive enough, or possibly by graphene sheeets, could be located very close for efficient removal of the photogenerated charges to an outside circuit. Many variations on this type of solar cell can be imagined. This project will be realized in close cooperation with experimental group of Proj.J. Michl, University of Colorado, Boulder, US).

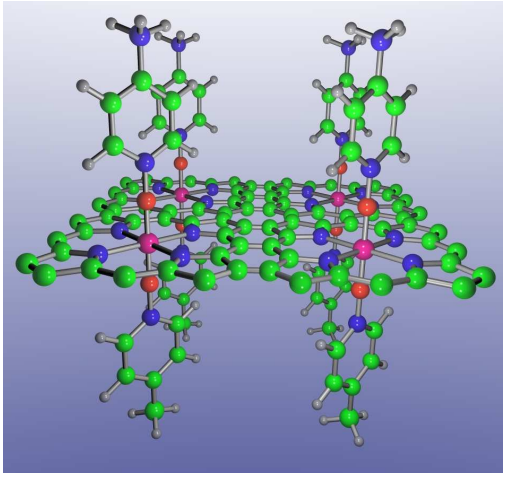

Figure 3. Porphene – cyclic analag of graphene. Modification of electronic structure by donors and acceptors; well defined pn junction; electrodes for efficient removal of charges to the outside circuits.

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4. Design of new catalytic materials for fuel cell feed gas purification

There is a rising economical, social, legal and ecological pressure to develop new, ecologically acceptable and efficient technological solutions without entailing excessive cost. Electrochemical energy conversion has been identified as one of the key technologies of the 21st century. In particular the direct transformation of chemical into electrical energy has received utmost attention. This transformation is realized in a fuel cell in which a fuel, such as a mixture of hydrogen and oxygen, is directly converted into electricity by means of an electro-catalytic process. Fuel cells, offer numerous advantages in comparison with other energy conversion and storage systems, such as high efficiency, high specific energy density, and ability to satisfy even demanding power requirements with little or no pollution. With respect to its promising prospects for applications in transportation, in particular the polymer electrolyte membrane fuel cells (PEMFCs) have received worldwide attention. Power sources/power plants ranging from 1 to 250kW have been built and operated. The performance of PEMFCs is higher than that of any other type of fuel cell. However, despite these promising prospects, several major technical challenges still remain. The energy conversion procedure is realized by supported metal particle (platinum and its alloys) catalysts. These catalytic materials are prone to deactivation (poisoning) by carbon monoxide (CO) contents in the fuel (feed gas). Minimizing CO poisoning at the anode is thus essential for use with hydrocarbon fuels such as natural gas or fuels produced in refinery plants from hydrocarbons and alcohols. Presented project aims at advancement of the catalysts that selectively remove CO from the hydrogen rich feed gas used for the PEMFC fuel cells. The research focus will be on the catalytic methanation (chemical conversion of CO into methane by reaction with hydrogen). Recently, it has been shown that Ruthenium nano-particle catalysts in zeolite materials present a very promising route to efficiently end selectively sustain the CO methanation reaction. Most importantly, particle size effects and metal charging effects were found to be crucial to the selectivity of the methanation. Especially, few atom ruthenium clusters were reported to be most selective in this reaction. Yet, a further improvement of the catalytic material fundamentally depends on a mechanistic understanding of the reaction. Advanced computational simulations at ICAST have proven to be a powerful means to reveal molecular aspects of metal catalyzed reaction mechanisms, and are the basis for the advancement of the efficiency of fuel cell technology as a green technology of the future. The project will be carried out in a close cooperation with the Institute for Surface Chemistry and Catalysis at the University of Ulm. This theme belongs to the priority research themes of the Science and Technology Park of the Split-Dalmatia County.

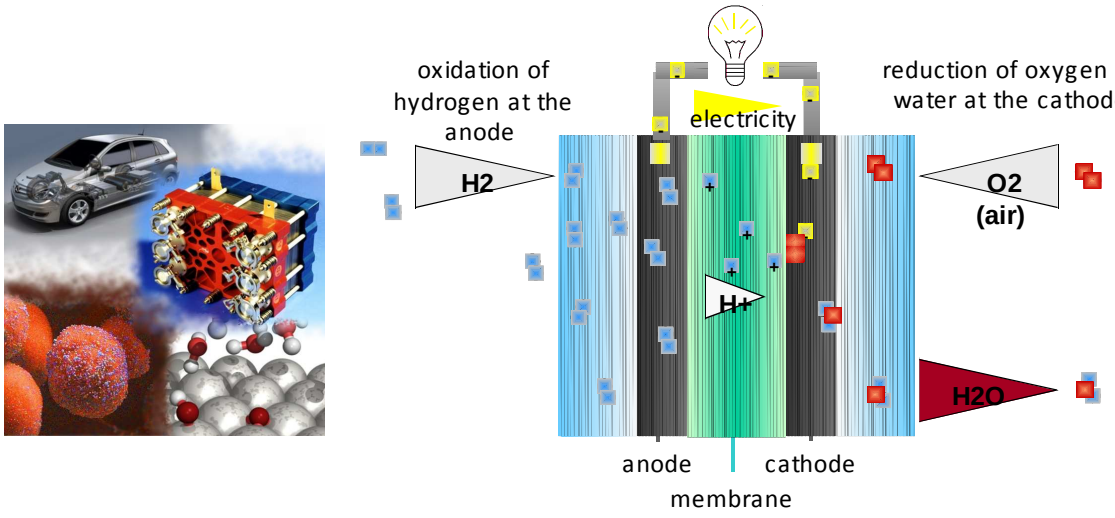

Figure 4. Proton Exchange Membrane Fuel Cell (PEMFC). Catalyst poison must be substantially reduced; selectivity for CO necessary.

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