



# Nanotechologies in Venice, Italy



Università Ca' Foscari, Venice, Italy - http://www.unive.it Veneto Nanotech, Italy - http://www.venetonanotech.it





VENETO NANOTECH ADMINISTRATION ADDRESS VENETO NANOTECH S.C.p.A. Via San Crispino, 106 35129 - Padova 049 7705500 http://www.venetonanotech.it

#### **VENETO NANOTECH DESCRIPTION**

Veneto Nanotech is a company established in 2003 by the Universities of Padua, Venice and Verona as well as by Veneto Region in cooperation with the Italian Ministry of University and Research (MIUR), several public institutions and private companies aiming at unifying the strategic vision of the Italian Nanotechnology Cluster.

Veneto Nanotech was established to coordinate the activities of the hi-tech cluster of nanotechnology, with the objective to build international excellence in research, to foster the application of nanotechnology, and to support the development of start-ups in the focus sector.

Its goal is to familiarize companies with nanotechnologies in order to promote process and product innovation as well as the creation of high-tech companies. It proposes itself as a link at an institutional level and as a referee for companies and research institutions, in order to create innovative hi-tech products. Furthermore, Veneto Nanotech aims at fostering and developing private investments in research and at supporting high-tech centres for the development of research projects and promotion of high-tech transfer.

## **VENETO NANOTECH ACTIVITIES**

#### Developing facilities and foster technology transfer

The Cluster plans and develops laboratories and research centres able to acknowledge the University resources and know-how and to focus on the themes of interest of the companies. The aim to use nanotechnology as a driver for the development of traditional companies has been delivered with a technology transfer strategy based on structures exclusively dedicated to technology transfer and use of public fund.

#### Support new entrepreneurship

Innovation is a bottom-up process too. The program supporting new start-ups is Nanochallenge. It is an International business plan competition for innovative ideas in Nanotechnology and Polymer-based materials, that provides two Grand Prizes of  $\in$  300.000 each as seed capital investment to create 2 new enterprises at least each year. The Nanochallenge objectives are to attract international high-value ideas in the Veneto Cluster and financial resources from venture capitalists, business angels and entrepreneurs and to strengthen the technological transfer and the positive relapse on the Italian and Veneto entrepreneurial system through pull actions.





#### Education, training and diffusion

Veneto Nanotech carries on several activities within education and training, collaborating with CIVEN, an association among the University of Padova, the University Ca' Foscari and IUAV of Venice and University of Verona.

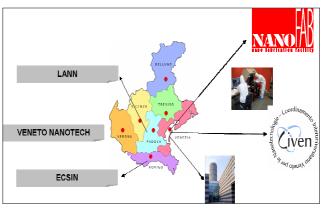
**ICN** – International Campus for Nanotechnologies – aims at representing a point of reference in the nanotechnology education, not only within the cluster but also nationwide and worldwide with different activities: Summer School; Interships/Felloship; nanotechnology dissemination activities and development of projects; center of education for schools (primary, middle and high schools) to promote the knowledge of nanotechnologies; specialized courses on the applications of nanotechnologies; professional training. The main activities organized every year are:

- The **International Master in Nanotechnology** is a post-graduate program that attracts brains from all the world. It is a necessary element of scientific growth of the District.
- Nanoweek is a training and diffusion event organised every year from Veneto Nanotech to promote nanotechnology in the region.

#### **RESEARCH FACILITIES**

Veneto Nanotech manages the following facilities operating in research activities:

**NanoFab** – Nanofabrication Facility – one of the first Italian research laboratories dealing with high-tech transfer to private companies. The laboratory's scientific focus concerns surface treatments using many deposition methods for new nano-structured and nanotreated materials, chemical and bio-chemical nanosensors development and microarrays. Nanofab strongly cooperates with CIVEN



and this guarantees the scientific development and coordination of the academic activities in the field of nanotechnologies (www.nanofab.it);

**ECSIN** – European Center for the Sustainable Impact of nanotechnologies – is an international centre and arises from the need to combine the NEST development with a proper knowledge of the impact of industrial processes and products upon the human being and the environment, according to an eco-sustainable development. The center aims at carrying out researches and studies to evaluate the effects due to the exposition to nanoparticles and/or nanomaterials on the human and environmental health.





It deals mainly with the risk assessment for companies, evaluation on nanoecotoxicology and juridical-sociological research linked to the use and/or exposition to nanoparticles and/or nanomaterials (www.ecsin.ue);

**LANN** – *Nanofabrication and Nanodevices Laboratory* – falls within the framework of a collaboration strategy among the VN Cluster, the University of Padua and CNR (National Research Council). This laboratory focuses on nanofabrication techniques for plasmonic devices, lab-on-a-chip systems, the research on bio-nanophotonics devices nanofabrication in the areas of nems, mems, lab-on-chip, cleantech. The facility will be open to third parties, where external R&D personnel will be able to do research on the basis of research proposals.

## **RESEARCH FIELDS**

Technology Platforms	Reasearch Projects	Technology Transfer	
Pvd - Pecvd	<ul> <li>Layers deposition, tribological properties, corrosion resistance</li> <li>Anti-reflecting surfaces</li> </ul>	<ul> <li>Coatings and layers for: glasses, mechatronics, sport system, automotive, aerospace</li> </ul>	
Sol - Gel	Thin films deposition	• Self-cleaning surfaces, protective nanocomposites, specific sensors, decorative surfaces	
Atmosferic Plasma	Surface treatments through atmosferic plasma	• Thin films deposition, polymeric substrates, fabrics and leather treatments	
Cold spray	Nanosctructured coating	<ul> <li>Coatings of metals</li> </ul>	
Electrochemical Sensors	<ul> <li>Nanostructures for sensors</li> </ul>	<ul> <li>Biosensors, electrochemical sensors</li> </ul>	
Biosensors and microarray	Microarray development	<ul> <li>Medical diagnostics, gene expression</li> </ul>	
Nanopowder	Light Alloys	<ul> <li>Automotive, mechanical parts, components</li> </ul>	
Polymers and nanostructures materials	Polymeric Systems	<ul> <li>Flexible and rigid packaging, sport system,</li> </ul>	
Environmental monitoring	Risk assessment	<ul> <li>Monitoring of work places, systems</li> </ul>	
Caracterization	Nano-metrology and certification of coatings		



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# SOME ACHIEVEMENTS SINCE 2009

Tech transfer activities	Total
Clients	140
Value of orders recieved (K euro)	3.540
Dimension of clients	
SMEs	98
Big enterprises	42
Business contacts	500
Feasibility study	
Numbers	300
Value (K euro)	10.550
Enterprises	300

Research activities	Total
Scientific publications	52
Presentations at scientific conferences	80
Scientific partnership	50
Research project started	25
Projects completed	10

People employed	Number	
Managers	5	
Administration	10	
Senior researchers	25	
Graduate students and scholarship holders	8	
Students	14	
Total	62	



#### **CA' FOSCARI UNIVERSITY IN VENICE**

#### **Historical profile**

Ca' Foscari University takes its Venetian name from the main university building, the Ca' Foscari (the Foscari house or palace), on the Grand Canal, between the Rialto and San Marco.

This palace was the seat of the Royal Higher Commercial College, founded on August 6, 1868 as Italy's first higher education institute to deal with economics and commerce. The idea of establishing such a school arose after the annexation of the Veneto to Italy in 1866, and was particularly promoted by Luigi Luzzatti. The College was the first institute of its kind to have as its primary objective the training of businessmen, but also to serve as a training college for secondary school teachers of commercial subjects.



Ca' Foscari main University building



Map of the Ca' Foscari University building in Venice

Since its foundation, the University has been housed in a remarkable fifteencentury palace on the Grand Canal. The School of Foreign Languages and Literatures was established in 1954, while the Faculties of Letters and Chemistry were created in 1969. In 1990, the latter finally became the present School of Science.

Various are now the buildings hosting the university premises throughout Venice (see Map).

At the moment, after the reorganization of the university academic structure implemented by the Italian Higher Education Reform, Ca' Foscari offers 30 first level and 43 second level degrees, 17 first level masters courses, 7 second level masters courses and 3 specializing courses offered by the School of Foreign Languages and Literatures, 16 doctoral research programs and a specializing program for secondary school teachers for a total of about 20,000 students. Ca' Foscari research facilities include a staff of about 1,000 people, out of which about 550 school members, 19 academic departments, 6 research centres, an efficient library system providing access to 700,000 books and 400,600 periodicals and an extensive network of PCs and workstations.



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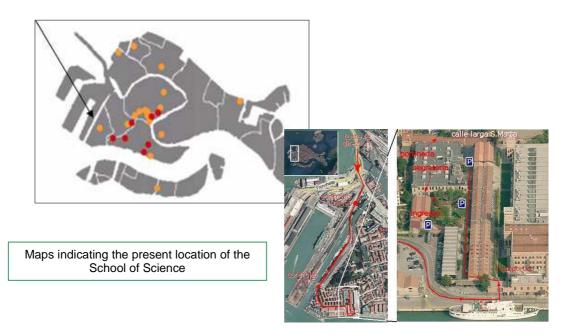


# The School of Science

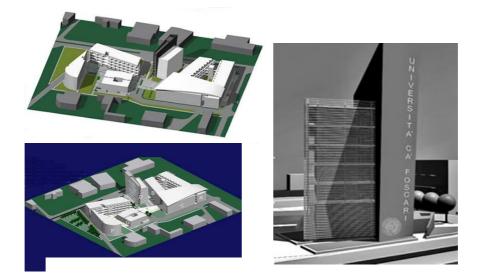
The School of Science hinges of three main subject areas:

Chemistry, with particular focus on <u>Material Science</u>, Environment and Information Technology

At the moment the School is located within Venice downtown:



A new campus is however under construction (completion expected by end of 2011) in the Venice mailand near Mestre (via Torino) very close to existing laboratories of material science and to the nanotech laboratories.



Future location of the School of Science in mainland (expected end 2011)





# **Research Groups Activities**

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# MATERIAL SCIENCE CHARACTERIZATION group

#### People:

Stefano Polizzi Pietro Riello Patrizia Canton Davide Cristofor Loris Bertoldo Tiziano Finotto Isidora Freris

Alvise Benedetti

Full Professor Associate Professor Associate Professor Assistant Professor Engineer(Microscopist) Technician Technician Post-Doc







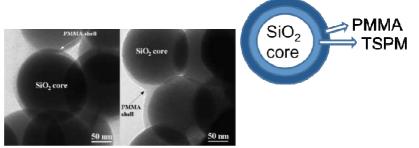


The research group has long-standing tradition in structural and morphological characterization, mainly by using X-ray powder diffraction (Rietveld analysis, line broadening analysis), smallangle X-ray scattering and electron microscopy (SEM and TEM). More recently, a synthesis laboratory was set out, mainly for inorganic materials.

## Research topics/Projects

#### Inorganic and hybrid nanomaterials with luminescent properties

Luminescent materials find widespread application in many different devices. We are particularly interested in bio-labelling and light harvesting for photovoltaic. Some materials in fact are very efficient in infrared (IR)-to-visible up-conversion with possible applications as IR-sensitive phosphors, biological labelling and solar cells. Other materials have up-converting properties, which may find application for harvesting the UV part of the solar sprectrum in photovoltaics.



The group is working on the synthesis of lanthanide-doped silica or zirconia nanoparticles or sol-gels, also using lanthanide containing organic molecules.

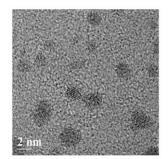
In this context the group is working on functionalized silica nanoparticles for producing polymers with enhanced mechanical properties and on their encapsulation in poly(methyl methacrylate) for non-toxic labelling particles or polymer films containing luminescent inorganic nanoparticles.





#### Metal supported catalysts

These materials are composed of metal nanoparticles dispersed in a porous matrix. The metal particles must be extremely small in order to maximize the number of surface atoms (the active one) per gram, due to the high costs of the precious metals used. For the same reason, agglomeration must be avoided. Often more than one metal is used, so that it is important to investigate the obtained phases (separate particles, alloys, solid solutions). Furthermore, the degree of order within the crystalline nanoparticles may influence the catalytic efficiency. All such morphological and structural parameters are studied by the research group by using XRD, SAXS (also in-situ using Synchrotron sources) and High Resolution TEM.



High Resolution TEM of Gold Nanoclusters

## Selected publications

- S. Sivestrini, P. Riello, I. Freris, D. Cristofori,,F. Enrichi, A.Benedetti <u>Structural and</u> <u>luminescence properties of europium(III)-doped zirconium carbonates and silica-</u> <u>supported Eu3+-doped zirconium carbonate nanoparticles J.Nanopart.Res</u>. in press DOI 10.1007/s11051-009-9655-5
- S. Piperno, Levi A. Gheber, P. Canton, A. Pich, G. Dvorakova, A. Biffis. <u>Microgel</u> <u>electrospinning: A novel tool for the fabrication of nanocomposite fibers</u> In: Polymer, 50 6193–6197 (2009)
- Freris, I.; Cristofori, D.; Riello, P.; Benedetti, A. <u>Encapsulation of submicrometer-sized</u> <u>silica particles by a thin shell of poly(methyl methacrylate</u>) In: J. Colloid Interface Sci. 331, 351-355 (2009)
- Dozzi M. V; Prati L; Canton P.; Selli E, <u>Effects of gold nanoparticles deposition on the</u> <u>photocatalytic activity of titanium dioxide under visible light</u>. In: Physical Chemistry Chemical Physics, 11, 7171-7180. (2009)
- M. Daldosso; D. Falcomer; A. Speghini; M. Bettinelli; S. Enzo; B. Lasio; Polizzi S., Synthesis, <u>Structural investigation and luminescence spectroscopy of nanocrystalline</u> <u>Gd3Ga5O12 Doped with lanthanide ions. In:</u> Journal of Alloys and Compounds, 451, 553-556 (2008)





- Canton P; Fazzini P. F; Meneghini C; Benedetti A.; Pozzi G. <u>Nanoscale</u> <u>Characterization of Metal Nanoclusters by Means of X-Ray Diffraction (XRD) and</u> <u>Transmission Electron</u>
- Microscopy (TEM) Techniques, In B. CORAIN; G. SCHMID; N. TOSHIMA, <u>Metal</u> <u>Nanoclusters in Catalysis and Materials Science: The Issue of Size Control - Part I,</u> AMSTERDAM, Ed. Elsevier, pp. 129-147. (ISBN 978-0-444-53057-8) (2008).
- Riello P.; Mattiazzi M; Pedersen J. S; Benedetti A. <u>Time-Resolved in Situ Small-Angle</u> <u>X-ray Scattering Study of Silica Particle Formation in Nonionic Water-in-Oil</u> <u>Microemulsions</u>. In: Langmuir, 24, 5225-5228. (2008).
- Enrichi F; Riccò R; Parma A; Riello P; Benedetti A., <u>Synthesis and characterization of</u> <u>monodisperse Eu-doped luminescent silica nanospheres for biological applications</u>, Conference Photonics Europe 2008, Strasbourg, France, 8 - 10 April 2008, In: Proceedings of SPIE - Volume 6991 <u>Biophotonics: Photonic Solutions for Better Health</u> <u>Care</u>, Jürgen Popp, Wolfgang Drexler, Valery V. Tuchin, Dennis L. Matthews, Editors, 69912E (May. 2, 2008), volume 6991, Cardiff, Ed. SPIE, 69912E-1-69912E-8
- R. Krsmanovic; V.A. Morozov; O.I. Lebedev; Polizzi S.; A. Speghini; M. Bettinelli; G. Van Tendeloo, <u>Structural and luminescence investigation on gadolinium gallium garnet</u> <u>nanocrystalline powders prepared by solution combustion synthesis</u>. In: Nanotechnology, 18, 325604-325612. (2007)
- Canton P.; M. Fichtner; C. Frommen; A. Leon, <u>Synchrotron X-Ray Studies of Ti-Doped</u> <u>NaAIH4</u>. In: Journal of Physical Chemistry. B, 110, 3051-3054. (2006).
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- Speghini A.; Bettinelli M.; Riello P.; Bucella S.; Benedetti A., <u>Preparation, structural</u> <u>characterization, and luminescence properties of Eu3+-doped nanocrystalline ZrO2</u>. In: Journal of Materials Research, 20 (10), 2780-2791 (2005)
- Bucella S; Riello P; Scremin B. F; Calvelli P; Polloni R.; Speghini A; Bettinelli M; Benedetti A, <u>Synthesis and Luminescence Properties of ZrO2 and ZrO2/SiO2</u> <u>Composites Incorporating Eu(III)-Phenanthroline Complex Prepared by a Catalyst-Free</u> <u>Sol-Gel Process</u>. In: Optical Materials, 27, 249-255 (2004)
- Corain B.; Centomo P.; Jerabek K.; Canton P., <u>Generation of size-controlled Pd0</u> <u>nanoclusters inside of the nanoporous domains of gel-type resins: diverse and</u> <u>convergent support to a strategy of "Template Controlled Synthesis".</u> In: Angewandte Chemie International Edition, 43, 959-962 (2004).





#### ELECTROANALYTICAL group

People:

Salvatore Daniele Maria A. Baldo Carlo Bragato Dario Battistel Full Professor Assistant Professor Technician Ph.D. student



#### Research topics

The group research activities are organised around the following themes:

Micro- and nano-electrodes: fabrication, characterisation and application; development of microelectrochemical sensors for food analysis and environmental applications; electrochemical measurements in non-conventional systems; nanostructured micro- and nano-electrodes.New materials and thin film technologies for development of microelectrode arrays and ensembles. Scanning electrochemical microscopy (SECM): Study, characterisation and modification of solid-liquid and gas-liquid interfaces at the micrometer level.

Numerical simulations of electrode reactions for reactions at the tip of the SECM

#### **Microelectrodes**

Microelectrodes have widened the applications of electroanalytical chemistry. Ranging from a few nanometres to a few micrometres, they improve the quality of experimental data and allow measurements in situations where conventional electrodes yield distorted responses. We fabricate and characterise microelectrodes having a variety of shape and dimensio down to tens of nanometers; perform electrochemical measurements in non-conventional systems, e.g. water in oil microemulsions, ionic liquids, wet soils; fruits; develop new analytical techniques and fabricate the SECM probes.

We have been also investigating properties of microdisc electrodes modified with nanoporous platinum films. These microelectrodes present the unique feature of having a large electroactive area (up to 1000 times greater than that of the bare electrode) while retaining the diffusional properties of conventional microdiscs. Such unique combination of properties is useful for redox processes involving an adsorption or absorption step. The modified electrode offers a huge number of active sites and its catalytic properties are significantly improved. This has been proved in the voltammetry of hydrogen peroxide. Also, alloying the Pt films with other metals such as bismuth, allows the dramatic improvement of electrocatalytical properties of the electrodes, towards small organic molecules (HCOOH, CH3OH) of interest in fuel cell applications.





#### Scanning electrochemical microscopy (SECM)

The scanning electrochemical microscope consists of a microelectrode held precisely in three dimensions by means of a micro-positioner. In the most conventional mode of operation, the current flowing to the microelectrode is recorded while scanning a few micrometers away from the surface under study. The instrument is akin to a high resolution chemical radar where a species electrochemically generated at the probe tip diffuses towards the substrate and interacts with its surface. The tip current reflects the tip-substrate distance and the electrochemical properties of the surface. It is thus possible to image the topography and the reactivity of surfaces. Although the best spatial resolution reported is around 20 nm, we aim to investigate electrochemical processes on the micrometre scale. The SECM is generally applied to the characterisation and modification of solid-liquid, liquid-liquid and liquid-gas interfaces at high resolution.

Our studies include, probing solid-solution interfaces of thin films made by nanocomposites (e.g. Pt-TiO2) with photocatalytic properties; studying the relationship between metal ion release and transport at water-soils interface, probing ion fluxes of redox species through porous ceramic films; studying localised corrosion and probing the dissolution of metal surfaces; probing catalyst activity towards the oxygen and hydrogen evolution processes. In recent years we have also focused on the modelling of the SECM response by using numerical simulations.

## Selected Publications

- Kicela, S. Daniele, <u>Platinum black coated microelectrodes for the determination of high</u> <u>concentrations of hydrogen peroxide</u>. In: Talanta, 68 (2006) 1632 – 1639
- M.A. Baldo, S.Daniele, <u>Voltammetric Monitoring and speciation of copper ions in Italian</u> <u>"Grappa" with platinum microelectrodes</u>.In: Electroanalysis, 18 (2006) 633 – 639.
- S. Daniele, E. De Faveri, I. Kleps, A. Angelescu, <u>Voltammetric characterization of</u> <u>micro- and submicrometer-electrode arrays of conical shape for electroanalytical use</u>.In: Electroanalysis 18 (2006) 1749 – 1756.
- G. Lindsey, G. Denuault, S. Daniele, E. De Faveri, <u>Scanning Electrochemical</u> <u>Microscopy: Approach curves for sphere-cap SECM tips</u>. In: Anal. Chem, .79 (2007) 2952 – 2956.
- S. Daniele, S. Bergamin, <u>Preparation and voltammetric characterisation of bismuth-</u> modified mesoporous platinum microelectrodes. Application to the electrooxidation of <u>formic acid.</u> In: Electrochem. Commun., 9 (2007) 1388 – 1393.



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- S. Hocevar, S. Daniele, C. Bragato, B. Ogorevic, <u>Reactivity at the film/solution interface</u> of ex-situ prepared bismuth film electrodes: A Scanning Electrochemical Microscopy (SECM) and Atomic Force Microscopy (AFM) investigation. In: Electrochim. Acta, 53 (2007) 555 – 560.
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- S. Daniele, M. A. Baldo, C. Bragato, <u>Recent Developments in Stripping Analysis on</u> <u>Microelectrodes</u>.In: Current Anal. Chem., 4 (2008) 215-228.





#### SOFT MATTER THEORY group

People:

Achille Giacometti Domenico Gazzillo Artem Badasyan Associate Professor Associate Professor Post-Doc



#### Research topics

The group is active in many branches of soft matter and complex fluids, using statistical physics tools such as numerical simulations, integral equation theory. Current main focus are on patchy colloids and biopolymers.

#### Self-Assembly of patchy particles

Next generation materials and devices composed of nanoscopic building blocks tailor-made for specific applications will not be fabricated via traditional methods. Rather they will attempt to mimic the precision and the reliability of biological self-assembly as a bottom-up process. This possibility has now emerged by an

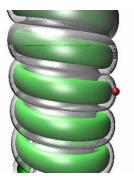


unprecedented development in particle synthesis which is creating a whole new set of colloidal particles, characterized by different patterns, particle patchiness and functionalities. Our group is investigating simple but realistically modeled patchy particle using a variety of different theoretical tools ranging from analytical mean-field theories to integral equation theories and highly sophisticated Monte Carlo simulations. Recent work deals with a particular model where the surface of a sphere is divided in two parts representing hydrophobic and polar parts of the surface groups. The hydrophobic part acts as an effective interaction among different spheres provided that they are properly aligned on the surface of the spheres. Those attractive parts (patches) can be either condensed into a single patch or distributed symmetrically on each spheres, thus providing a remarkable flexibility to the model. Within this framework, we have been able to provide a detailed investigation of the phase diagram and structural properties.





#### Emergence of secondary structures in tube-like polymers in a solvent



Protein are co-polymers built from some 20 amino acids linked together into a linear polipeptide chain having a large number of repeated units each of which bears a (generally different) side chain. A knowledge of the 3D structure of a protein is necessary to understand how it functions.

One of the fascinating feature of protein structure is that they have a natural hierarchy of level of description. Chemical bonds fixing the sequence of amino acids in protein chain gives rise to the so-called

"primary structure" of a protein. This microscopic description is of course necessary when dealing with the detailed biochemical processes occurring in their synthesis and formations. Non-covalent interactions (having strengths of the order of thermal energy) maintain the 3D architecture are complex and of great diversity. In spite of this, there exist a set of "recurrent motifs" which are "non-specific", notable examples being the alpha helices and beta strands, and these recurrent motifs form the so-called "secondary structure". At an even coarser-grained level, the three-dimensional structure of a folded protein form a globule constituting the "tertiary structure".

The origin of simple forms appearing in the protein architectures can be traced back to the details of microscopic interactions of the constituent atoms and the quantum chemistry that governs their assembly. On the other hand, the common use by nature of these modular structure begs for a simple unified explanation for their ubiquity.

We are currently investigating the solvation properties of a simple model (a "thick" polymer) which has been shown to provide a remarkable precise description of the emergence of secondary structures in a protein.

Selected publications:

- A.Giacometti, G. Pastore and F. Lado, <u>Liquid-vapor coexistence in square-well fluids: a</u> RHNC study In: Molec. Phys. 107, 555-562 (2009)
- A. Giacometti, F. Lado, J. Largo, G. Pastore and F. Sciortino, <u>Phase diagram and</u> <u>structural properties of a simple model for one-patch particles</u>, In: J. Chem. Phys. 131, 174114-1/174114-13 (2009)
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- A.V. Badasyan, A. Giacometti, Y. Sh. Mamasakhlisov, V.F. Morozov and A.S. Benight, <u>Microscopic foundation of the Zimm-Bragg model</u>. In: Phys. Rev. E submitted (2009)



 F. Sciortino, A. Giacometti and G. Pastore, <u>Phase diagram of Janus Particles</u>. In: Phys. Rev. Lett. 103, 237801-1/237801-4 (2009) , Featured in the cover (issue 23, 4 december 2009), Featured in Nature Research Highlights, Vol. 462, 17 December 2009, page 828

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- C. Poletto, A. Giacometti, A. Trovato, J.R. Banavar and A. Maritan, <u>Emergence of Secondary Motifs in Tube-Like Polymers in a Solvent</u>. In: Phys. Rev. E 77, 061804 (2008), Selected for the Virtual Journal of Biology Physics Research, Vol. 16, Issue 1, July 1 (2008)
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#### Laboratory of SENSORS FOR ELECTROCHEMISTRY

People:

Paolo Ugo Ligia M. Moretto Morena Silvestrini Michael Ongaro Full Professor Assistant Professor Ph.D student Ph.D student



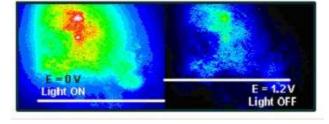
#### Research topics/Projects

The research activity of the **Laboratory of Sensors for Electrochemistry** – LSE - group is focused on the preparation and characterization of electrodes modified with polymers, nanoelectrodes for sensors application and nanomaterials for electrochemistry. The main research topics are: nanoelectrochemical sensors, modified electrodes, membrane template nanomaterials

## A. Functional ultrathin coatings on electrodes

The LSE group contributed significantly to the development of the so called ion exchange voltammetry (IEV). This technique uses electrodes modified with thin layer of ionomers for the selective analysis of redox ions at submicro and subnanomolar concentration levels.

Recently LSE applied the Langmuir-Blodgett technique for the deposition of ultra thin layer (with thickness of a few nanometers) of ionomers, such as Nafion, on electrodes surfaces. The modified electrodes obtained were applied for the immobilization of molecules of interest as redox mediators in biosensors or as electrocatalyst. The immobilization of luminophores inside the film was exploited to study the film morphology.



Electrochemical switching of light at Nafion LB films





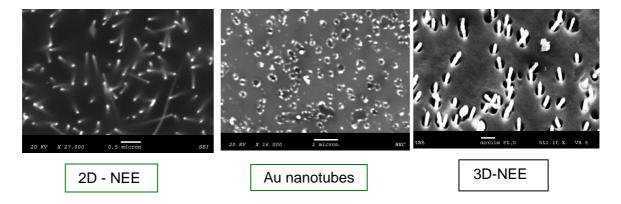
Research is in progress to develop sensors able to apply electrochemiluminescence (ECL) of  $Ru(bpy)_3^{2+}$  to the determination of biologically interesting analytes, (alkylamines, oxalate, aminoacids etc.).

# B. Nanoelectrodes and nanoelectrochemistry

Since 1996, the LSE group have been involved in the preparation, characterization ed sensing application of nanoelectrodes ensembles (NEEs). NEEs are nanotech based electroanalytical tools which find application in a variety of fields ranging from electroanalysis to sensors and electronics. They are fabricated by growing metal nanowires in the pores of a template, typically a polycarbonate porous membrane. The density of the pores in the template determines the density of the nanoelectrodes (typically 109 nanoelectrodes/ cm2) while the diameter of the pores determines the diameter of each nanoelectode (typically 30-40 nm). NEEs are characterized by signal/background current ratios up to 1,000 times higher than regular electrodes so that detection limits at NEEs are improved from 2 to 3 orders of magnitude with respect to regular electrodes. We can prepare NEEs in the form of ensembles of nanodisk or nanowire electrodes. Functionalization of the NEEs allowed us the preparation of electrochemical sensors (e.g. for  $H_2O_2$  or glucose).

We are presently developing NEE based immunosensors for the detection of a protein, namely the HER2 receptor. The determination of the expression levels of the HER2 receptor and the binding activity of its agonist trastuzumab (or Herceptin<sup>®</sup>) constitute a very actual issue, since trastuzumab is used in the adjuvant therapy of breast cancer.

The possibility to detect HER2 is extremely important for the identification of cancers that can be treated with Herceptin<sup>®</sup>, providing a good opportunity to define the so-called personalized therapies.







## Selected publications

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- M. Zamuner, D. Talaga, F. Deiss, V. Guieu, A. Kuhn, P. Ugo, N. Sojic, <u>Fabrication of a</u> <u>macroporous microwell array for surface-enhanced Raman scattering</u>, In: Advanced Functional Materials 19, 3129-31350 (2009)
- M. Zamuner, S. Pozzi Mucelli, M. Tormen, G. Stanta, P. Ugo <u>Electrochemical</u> <u>nanobiosensors and protein detection</u>, In: European Journal of Nanomedicine, 1, 33-36 (2008)
- L.M. Moretto, T. Kohls, A. Chovin, N. Sojic, P. Ugo Epifluorescence imaging of electrochemically Switchable Langmuir-Blodgett films of Nafion, Langmuir, 24, 6367-6374 (2008)
- S. Pozzi Mucelli, M. Zamuner, M. Tormen, G. Stanta, P. Ugo Nanoelectrode ensembles as recognition platform for electrochemical immunosensors, Biosensors & Bioelectronics, 23, 1900-1903 (2008)
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## EXPERIMENTAL PHYSICS OF MATERIALS

People:

Giancarlo Battaglin Francesco Gonella Elti Cattaruzza Enrico Trave Full Professor Associate Professor Assistant Professor Assistant Professor



## Research topics/Projects

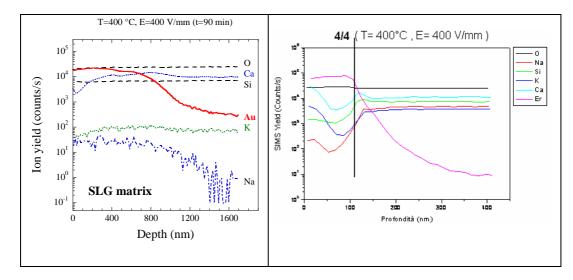
Doping of silicate glasses

Silicate glass layers are doped with either transition metals (Ag, Cu, Au, Co, Cr...) or rare-earths (Er...) by conventional thermal ion-exchange or by a field-assisted solid-state ion exchange, in which a metallic or oxide film of the dopant is first deposited on a glass slide by rf-sputtering, and then made penetrating by applying an electric field across the sample, at temperatures below the glass softening point. In this way, dopant may be incorporated in the glass matrices well above their solubility limit (with surface concentration values up to 10<sup>21</sup> atoms/cm<sup>3</sup>), so creating layers with prescribed properties, with application in the fields of photonics and optoelectronics materials, optical waveguides, magnetic materials and sensors. In particular, by the field-assisted process, also multivalent ions can penetrate into the glass, with the final aim at controlling their state and their possible aggregation inside the matrix. The diffusion process is also studied from the point of view of the transport phenomena modeling, since the diffusion involves local field build-up, interference phenomena (pseudo-mixed alkali effect) and significant local re-arrangements of the glass matrix. The process is also used as the first step of combined methodologies for promoting the controlled aggregation of the dopants in form of nanoclusters, by means of ion irradiation, laser irradiation, or heat treatments in selected atmospheres. In the figure below, secondary ion mass spectrometry diffusion profiles are shown for a gold-doped (left) and an erbium-doped (right) sample.





The group performs also optical experiment for the determination of the non-linear refractive index,  $n_2$ , by means of the Z-scan technique, with a low repetition rate laser in the picoseconds regime.



Diffusion profiles, obtained by secondary ion mass spectrometry, are shown for a golddoped (left) and an erbium-doped (right) soda-lime glass samples synthesized by fieldassisted solid-state ion exchange

Thin films deposition by radio-frequency magnetron co-sputtering

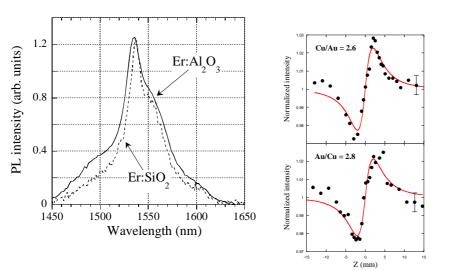
For the thin film synthesis we use a radio-frequency magnetron sputtering apparatus equipped with three sources which can be operated independently and contemporarily. The sample holder can be heated up to 500 °C, rf-polarized, and can rotate around its axis to ensure uniform deposition conditions (better than 5% over the surface of a disk 10 cm in diameter). Using this apparatus, we are able to synthesize thin films of a single species, multilayers (by sequential deposition) and mixtures (or alloys or compounds) of two or three different species (by co-deposition), in ultra high base-vacuum conditions thus ensuring a very low level of contaminants. In the deposition process critical parameters can be varied in a controlled manner, i.e., the power supplied to each source, the pressure and the composition of the gas plasma (reactive sputtering is possible) and the sample temperature, in order to obtain different structures for the same sample composition, or a wide range of composition for the same species.

Our current research interests span over the synthesis of thin films suited for hydrogen storage applications (Mg-based), electrocatalysis (IrO<sub>2</sub>- and RuO<sub>2</sub>-





based), photonics (metal nanocluster composite glasses and Er-doped silica and alumina) and magneto-plasmonics (silica containing nanoclusters of both magnetic metals and metals with suitable plasmonic features).



On the left: near-infrared photoluminescence spectrum, obtained by Ar laser excitation at 488 nm, for Er-doped silica films and Erdoped alumina films deposited by radiofrequency magnetron cosputtering.

On the right, corrected Z-scan far field curves for two thin films of silica with embedded Au-Cu alloy nanoparticles with symmetrical Au/Cu value, showing a positive nonlinear refractive index (the films were synthesized by by radiofrequency magnetron cosputtering).

#### Selected recent publications

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#### **GREEN CHEMISTRY FOR SUSTAINABILITY**

#### People:

Maurizio Selva Alvise Perosa Vittorio Lucchini Massimo Fabris Marco Noè Associate Professor Assistant Professor Full Professor Ph.D. Student Ph.D. Student



#### General

Chemistry is often perceived as dangerous and dirty, although the chemical industry is one of the primary providers of well-being for the world population in the form of consumer goods. Our goal is to tackle some of the environmental and safety issues facing chemical production by molecular design, i.e. by understanding transformations at the molecular level, and by designing alternative chemical routes that will improve sustainability.

The green chemistry group operates at the interfaces of the chemistry and environmental sciences departments of Ca' Foscari University in Venice. Research is aimed at the design and implementation of new synthetic methodologies using clean reagents and solvents and new chemical (catalytic) processes with reduced impact on health, safety, the environment, and energy. In short: green chemistry!

## Expertise

- 1) Non-conventional green(er) reaction media for organic syntheses: Green solvents, Multiphase liquid systems, Solvent free reactions
- 2) New green organic reagents: Alkyl carbonates, Platform chemicals from biomass
- 3) (More) sustainable synthetic methodologies: Atom economic, Catalytic, Recyclable materials

#### Examples of project areas

- 1. Green synthesis and characterization of new ionic liquids
- 2. Design of ionic liquids as tunable organo-catalysts
- 3. Green(er) carbon-carbon bond forming reactions
- 4. Olefin metathesis with heterogeneous catalysts in scCO<sub>2</sub> and.
- 5. Glycerol and glycerol carbonate as organic building blocks
- 6. Alkylation of nucleophiles using organic carbonates
- 7. Ball milling reactions in the synthesis of polymer intermediates
- 8. Ionic liquids as templating fluids for organic syntheses
- 9. Kinetic and mechanistic studies using advanced NMR techniques
- 10. Pharma intermediates using green synthetic methodologies





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- M. Selva, A. Perosa, M. Fabris, P. Canton., <u>The Metathesis of a-Olefins over Supported</u> <u>Re-Catalysts in Supercritic al CO<sub>2</sub>, In: Green Chem</u>, 11,229-238 (2009)
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- M. Selva, P. Tundo, D. Brunelli, A. Perosa., <u>Chemoselective Reactions of Dimethyl</u> <u>Carbonate Catalysed by Alkali Metal Exchanged Faujasites: the Case of Indolyl</u> <u>Carboxylic Acids and Indolyl Substituted Alkyl Carboxylic Acids</u>, In: Green Chem, 9, 463-468 (2007)
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- J. DeSimone, M. Selva, P. Tundo, <u>Nucleophilic Displacements in Supercritical Carbon</u> <u>Dioxide using Silica Supported Phase-Transfer Agents</u>, In : J. Org. Chem, 66, 4047-4049 (2001)





## PREPARATION AND CHARACTERIZATION OF NEW INORGANIC MATERIALS

#### People:

Loretta Storaro Aldo Talon Martina Marchiori Elisa Moretti

Maurizio Lenarda

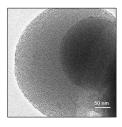
Full Professor Assistant Professor Graduated Technician Technician Post-Doc



## Research topics/Projects

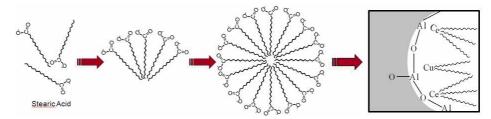
The Research Unit has a wide experience in the preparation of nanostructured materials derived from layered oxides, cationic natural and synthetic clays and in the structural

modifications of synthetic clays obtained by hydrothermal processes. The group has a wide scientific production on the process of pillaring clays, by the introduction of AI and Ti poly-oxo-cations, doped with suitable elements (in particular Ce and Mg) in order to give to the material peculiar acid-base or redox characteristics or, in the case of ion exchange with noble metal ions, the necessary properties to promote the



catalytic activity. The unit is very active in the synthesis and characterization of MCM-41and MSU type mesoporous oxides, with an ordered network of silica or silica-alumina, doped if necessary with Zr or Sn.

 $AI_2O_3$  with ordered mesoporosity and doped with suitable metals (Cu, Ce, Pd, Zn) is another class of porous materials obtained by a surfactant-assisted one-pot synthesis, using aluminum alkoxides as Al source and metal stearates both as metal precursors and templates of the inorganic matrix.





The unit is now active in the design, preparation and physico-chemical characterisation of nanostructured catalysts based on transition metals supported on low dimensional oxides derived from hydroxide and oxide precursors with a layered structure. In particular, catalytic systems obtained from nanometric level manipulations of layered perovskites

are studied. The Unit carries out studies of the catalytic reactivity of the heterogeneous systems, in batch and in flow, both in liquid and in vapour phase. In particular it studies the water-gas shift





reaction, the hydrogen production for renewable resources and its purification by preferential CO oxidation.

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- M. Turco, C. Cammarano, G. Bagnasco, E. Moretti, L. Storaro, A. Talon, M. Lenarda, <u>Oxidative methanol steam reforming on a highly dispersed CuO/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst prepared by a single-step method, In: Appl. Catal. B: Environmental 91 (2009) 101.
  </u>
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