CNPEM

São Paulo School of Advanced Sciences on

Recent Developments in Synchrotron Radiation

July 13th - 24th, 2015, Campinas, Brazil

http://pages.cnpem.br/synclight2015

APS physics FAPESP LNLS CNPEM

Ministry of
Science, Technology
and Innovation

BRAZILIAN GOVERNMENT
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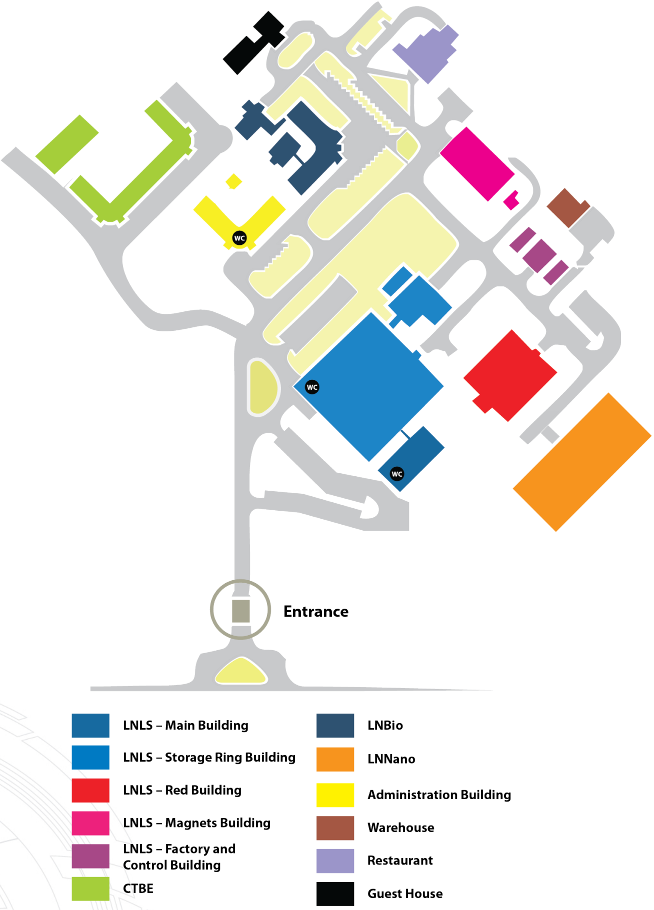
CNPEM - Campus Map



The lectures are going to be held in the LNLS Auditorium at the Storage Ring Building.

SyncLight 2015: the São Paulo School of Advanced Sciences (ESPCA) on Recent Developments in Synchrotron Radiation

SyncLight 2015 is bringing together students and young researchers (MSc, PhD and Post-doc fellows) from Brazil and from many other countries.

The main goal of this School is to present what synchrotron light offers in the form of new tools for their research. We intend to show that there are numerous new possibilities that appeared in the last decade, particularly those exploring bright nanometer size x-ray beams and coherence. Taking that into consideration, the school instructors were selected from currently active and leading researchers around the world.

This school will provide training for the students in the fields of physics, chemistry, biology, geosciences, medicine and materials science engineering, among others. The specific interdisciplinary character of the school will contribute to fruitful exchanges between researchers belonging to these different disciplines.

SyncLight 2015 is being promoted jointly by CNPEM (Brazilian Center for Research in Energy and Materials), LNLS (Brazilian Synchrotron Light Laboratory) and APS (American Physical Society), and it's supported by FAPESP (São Paulo State's Research Foundation).

The chosen venue seems particularly appropriate because LNLS is currently engaged in the development and construction of Sirius, the next Brazilian synchrotron light source. It is planned to be a state-of-the-art machine, designed to be one of the brightest in the world. A new generation of users and developers are needed to exploit this new source that will be operating in 2018.

São Paulo School of Advanced Sciences

SyncLight 2015 is supported by FAPESP (São Paulo State's Research Foundation) as part of the "São Paulo School of Advanced Sciences (ESPCA)"program, which offers courses on advanced science and technology, contributing to the academic development of the participants.

Through the ESPCA, FAPESP offers funding for the organization of short duration courses (around 2 weeks) in the different areas of knowledge in São Paulo State.

The ESPCA lecturers are scientists from many different countries and also from Brazil, with excellent qualification and prominence in their research fields. Through this initiative FAPESP expects to establish, in the State of São Paulo, a globally competitive hub for talented researchers.

CNPEM: A cutting-edge research center

Welcome to the Brazilian Center for Research in Energy and Materials (CNPEM), a world-class center for development of science, composed by four laboratories: Brazilian Synchrotron Light Laboratory (LNLS), Brazilian Biosciences National Laboratory (LNBio), Brazilian Bioethanol Science and Technology Laboratory (CTBE) and Brazilian Nanotechnology National Laboratory (LNNano).

Located in Campinas (SP), CNPEM is a private nonprofit organization qualified by the Ministry of Science, Technology and Innovation (MCTI), whose laboratories have open facilities to the scientific and industrial communities across the country and abroad.

Aerial photograph of CNPEM campus with artistic view of the Sirius building

Brazilian Synchrotron Light Laboratory (LNLS)

As part of CNPEM, the **Brazilian Synchrotron Light Laboratory (LNLS)** is responsible for operating the only synchrotron light source in Latin America, providing high brilliant light from infrared to X-rays for the analysis of organic and inorganic materials.

Designed and built with Brazilian technology, LNLS was inaugurated in 1997 and, since then, it offers unique conditions to the progress of synchrotron techniques at this region. Today, its synchrotron light source has 17 experimental stations (beamlines), where research proposals can be conducted.

The scientific community will soon get reinforcement for researches that rely on synchrotron light. This is because LNLS is currently engaged in the development and construction of **Sirius**, a latest generation synchrotron light source that will open new experimental possibilities in several areas of research.

Planned to be one of the most advanced light sources in the world, it will open up new perspectives for research in many fields, such as material science, structural biology, nanoscience, physics, earth and environmental science, cultural heritage and many others.

Sirius is scheduled to start commissioning in 2018 and to be opened to users in 2019, with potential to elevate Brazil to a higher and more competitive level in scientific research.

Organizers | Scientific Committee

Hélio Cesar Nogueira Tolentino (CNPEM/LNLS, Brazil) - **Event Coordinator**
Esen Ercan Alp (Argonne National Laboratory, USA)
Harry Westfahl Junior (CNPEM/LNLS, Brazil)

Local Committee

Adriana Semeghini – CNPEM/LNLS
Graziela Esteves - CNPEM/LNLS
Ildéria Santos - CNPEM/LNLS
Luciana Noronha – CNPEM/LNLS
Pâmela Machado – CNPEM/LNLS
Tatiane Cortes – CNPEM/LNLS

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13th July 2015

08:15 - 08:45	**Registration at LNLS**
08:45 - 09:00	**Welcome**
09:00 - 09:30	**Antonio José Roque da Silva (Director of LNLS)** ↗ Presentation of the Brazilian Synchrotron Light Laboratory
09:30 - 10:00	**Carlos Henrique de Brito Cruz (FAPESP Scientific Director)** ↗ Presentation of FAPESP (São Paulo Research Foundation)
10:00 - 11:00	**Coffee break**
11:00 - 12:00	**Liu Lin – LNLS (Brazil)** Introduction to synchrotron radiation and forth generation storage rings
12:00 - 13:00	**Dennis Mills – APS Argonne (USA)** ↗ Synchrotron Radiation Sources and X-Ray Optics – 1
13:00 - 14:30	**Lunch**
14:30 - 15:30	**Aldo Craievich – USP (Brazil)** ↗ Introduction to X-Ray Diffraction and Scattering
15:30 - 16:30	**Pieter Glatzel – ESRF (France)** ↗ Introduction to X-Ray Spectroscopies
16:30 - 17:30	**Cinzia Giannini – CNR (Italy)** ↗ From Crystallography to Imaging
17:30 - 19:00	**Welcome reception**

14th July 2015

09:00 - 10:00	**Dennis Mills – APS Argonne (USA)** ↗ Synchrotron Radiation Sources and X-Ray Optics – 2
10:00 - 10:45	**Coffee Break**
10:45 - 11:45	**Ian Robinson – UCL (UK)** ↗ Bragg Coherent Diffraction Imaging
11:45 - 12:45	**Jianwei Miao – UCLA (USA)** ↗ Imaging at the X-ray Frontier: Coherent Diffractive Imaging for Physical and Biological Sciences – 1
12:45 - 14:00	**Lunch**

14:00 - 16:30	**Poster session**
16:30 - 19:00	**Social event at the kiosk**

15th July 2015

09:00 - 10:00	**Jianwei Miao – UCLA (USA)** ↗ Imaging at the X-ray Frontier: Coherent Diffractive Imaging for Physical and Biological Sciences – 2
10:00 - 10:45	**Coffee Break**
10:45 - 11:45	**Cinzia Giannini – CNR (Italy)** ↗ X-ray Diffraction and Imaging of Smart Nanomaterials
11:45 - 12:45	**Ian Robinson – UCL (UK)** ↗ Experience with X-ray Ptychography
12:45 - 14:00	**Lunch**
14:00 - 18:00	**Tutorials at the beamlines**

16th July 2015

09:00 - 10:00	**Ercan Alp – APS Argonne (USA)** ↗ Inelastic X-Ray Scattering-Principles and Applications – 1
10:00 - 10:45	**Coffee Break**
10:45 - 11:45	**Pieter Glatzel – ESRF (France)** ↗ X-ray inelastic scattering in catalysis
11:45 - 12:45	**Daniela Zanchet – Unicamp (Brazil)** ↗ X-ray scattering and absorption in Catalysis
12:45 - 14:00	**Lunch**
14:00 - 18:00	**Tutorials at the beamlines**

17th July 2015

09:00 - 10:00	**Ercan Alp – APS Argonne (USA)** ↗ Inelastic X-Ray Scattering-Principles and Applications – 2
10:00 - 10:45	**Coffee Break**

10:45 - 11:45	**Eduardo Granado – Unicamp (Brazil)** ↗ Novel magnetic and superconducting materials investigated by X-ray diffraction and spectroscopy at LNLS
11:45 - 12:45	**Narcizo Souza Neto – LNLS (Brazil)** ↗ Rare-earths under high pressure
12:45 - 14:00	**Lunch**
14:00 - 18:00	**Tutorials at the beamlines**
	18th July 2015
10:00 - 11:00	**Mario Murakami – LNBio (Brazil)** ↗ Structural Biology
11:00 - 12:00	**Julio Criginski Cezar – LNLS (Brazil)** ↗ Soft X-Ray Spectroscopy at LNLS
12:30 - 17:00	**Barbecue at LNLS**
	19th July 2015
-	**Free day**
	20th July 2015
09:00 - 10:00	**Andrea Dessen – CNRS (France)** ↗ Synchrotron data collection and analysis of biological macromolecules – 1
10:00 - 10:45	**Coffee Break**
10:45 - 11:45	**Maria Carmem Asensio – Soleil (France)** ↗ Angle Resolved Photo Emission Spectroscopy, ARPES – 1
11:45 - 12:45	**Ruben Reininger (APS)** ↗ X-Ray optics simulations and current developments on software packages – 1
12:45 - 14:00	**Lunch**
14:00 - 18:00	**Tutorials at the beamlines**
	21st July 2015
09:00 - 10:00	**Daniel Haskel – APS Argonne (USA)** ↗ Magnetism/high pressure with X-rays – 1

10:00 - 10:45	**Coffee Break**
10:45 - 11:45	**Andrea Dessen – CNRS (France)** ↗ Synchrotron data collection and analysis of biological macromolecules – 2
11:45 - 12:45	**Ruben Reininger (APS)** ↗ X-Ray optics simulations and current developments on software packages – 2
12:45 - 14:00	**Lunch**
14:00 - 18:00	**Tutorials on the beamlines**

22nd July 2015

09:00 - 10:00	**Daniel Haskel – APS Argonne (USA)** ↗ Magnetism/high pressure with X-rays – 2
10:00 - 10:45	**Coffee Break**
10:45 - 11:45	**Maria Carmen Asensio – Soleil (France)** ↗ Angle Resolved Photo Emission Spectroscopy, ARPES – 2
11:45 - 12:45	**Donald Sparks – University of Delaware (USA)** ↗ X-Rays in Soil Science – 1
12:45 - 14:00	**Lunch**
14:00 - 18:00	**Tutorials at the beamlines**

23rd July 2015

09:00 - 10:00	**Simo Huotari – University of Helsinki (Finland)** ↗ X-Ray Raman Spectroscopy and Imaging – 1
10:00 - 10:45	**Coffee Break**
10:45 - 11:45	**Ryan Tappero – NSLS (USA)** ↗ Introduction to Techniques and Environmental Science Applications of Synchrotron X-ray Fluorescence Microprobes – 1
11:45 - 12:45	**Donald Sparks – University of Delaware (USA)** ↗ X-Rays in Soil Science – 2
12:45 - 14:00	**Lunch**

14:00 - 18:00	**Visit to Unicamp**
	24th July 2015
09:00 - 10:00	**Ryan Tappero – NSLS (USA)** ↗ Introduction to Techniques and Environmental Science Applications of Synchrotron X-ray Fluorescence Microprobes – 2
10:00 - 10:45	**Coffee Break**
10:45 - 11:45	**Dalton Abdala – LNLS (Brazil)** ↗ X-ray spectroscopy in soils
11:45 - 12:45	**Simo Huotari – University of Helsinki (Finland)** ↗ *X-Ray Raman Spectroscopy and Imaging – 2*
12:45 - 14:00	**Lunch**
14:00 - 18:00	**Evaluation and closing remarks** Evaluation and departures to Guarulhos (GRU) and Viracopos (VCP) airports

São Paulo School of Advanced Sciences on

Recent Developments in Synchrotron Radiation

July 13th - 24th, 2015, Campinas, Brazil

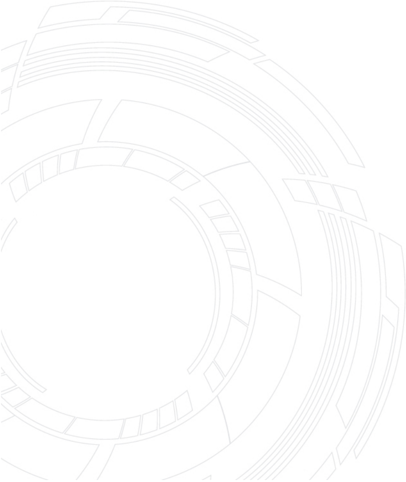
LECTURES

Liu Lin
Brazil
Centro Nacional de Pesquisa em Energia e Materiais – CNPEM
Laboratório Nacional de Luz Síncrotron – LNLS

Lecture:
Introduction to synchrotron radiation and forth generation storage rings

Dennis M. Mills
USA
Argonne National Laboratory
Advanced Photon Source (APS)

Lectures:
Synchrotron Radiation Sources and X-Ray Optics (I and II)



Aldo Craievich
Brazil
University of São Paulo – USP
Institute of Physics

Lecture:
Introduction to X-Ray Diffraction and Scattering

(i) Basic theory of X-ray diffraction by crystalline materials. Connection between electron density and diffraction amplitude. Experimental setups. Ewald contruction. Single crystal and powder methods. Determination of the structure of crystalline materials. The phase problem.
(ii) X-ray diffuse scattering by imperfect crystals and by amorphous structures. Pair distribution function.
(iii) Low resolution techniques and structural studies at the nanometric scale. Transmission and grazing incidence small-angle X-ray scattering. Basic theory.
(iv) Some applications of synchrotron X-ray scattering to materials and biological sciences.

Pieter Glatzel
France
European Synchrotron Radiation Facility – ESRF

Lectures:
Introduction to X-Ray Spectroscopy X-ray inelastic scattering in catalysis

Cinzia Giannini
Italy
National Research Council – CNR
Institute of Crystallography – IC

Lecture:
From Crystallography to Imaging

From the discovery of X-ray diffraction in 1912 by M. Laue, W. Friedrich, P Knipping, and from the first crystal structure determination in 1913 by W. H. and W.L. Bragg (father and son) more than 30 nobel pizes were awarded for works related to X-ray Crystallography in chemistry, physics, medicine and biology. Crystallography allowed and still allows to discover the most invisible secrets of the world around us, which can been explored down to atomic resolution. One limit only: the need for a crystal, namely a regular 1D or 2D or 3D arrays of atoms/molecules extended for few nanometers (nanocrystals), micrometers (microcrystals) or even millimeters. Crystals are familiar to us (salt, aspirin, precious stones etc) and many of their structures have been determined so far with X-ray Crystallography. However, biologic matter is largely non crystalline or only partially crystalline. For example, the mineral component of our bones is made of hydroxyapatite nanocrystals, or collagen in several human tissues forms fibers, which can be considered as 1D crystals. In these cases, X-ray diffraction patterns contain characteristic structural or morphological features which can be measured and transformed into quantitative microscopies, making this technique an effective tool for i) the engineering of a smart tissue, ii) the design of a novel drug or iii) the diagnosis of a specific pathology.

Nowadays, matter can be imaged with X-rays at different length scales and with several imaging techniques, the more and more efficiently thanks to the recent advent of high-brilliance X-ray sources, the fabrication of X-ray focusing optics and the appearance of novel high-performances detectors. When relying on the presence of distinctive structural properties in the X-ray diffraction pattern, incoherent X-ray beams are sufficient. If dealing with completely disordered specimens (such as recalcitrant proteins not readily crystallizable) coherent X-ray beams are today available. In this latter case, a revolution is going on with the novel third and fourth generation X-ray sources. Through them, the complex and costly methods of crystallization, studied so far to achieve reasonably pure and defect free protein crystals, with the dimensions and quality required for a diffraction study at atomic resolution, are destined to become just an obsolete need.

In this lesson an introduction to some X-ray Imaging techniques will be given, focusing on scanning X-ray micro imaging studies related to the bio and nanomedicine world.

Ian Robinson
UK
UCL – London Centre for Nanotechnology
Faculty of Maths & Physical Sciences

Lectures:
Bragg Coherent Diffraction Imaging
Experience with X-Ray Ptychography

Jianwei (John) Miao
USA
University of California – UCLA
Department of Physics & Astronomy and California NanoSystems Institute
miao@physics.ucla.edu

Lecture:
Imaging at the X-ray frontier: Coherent Diffractive Imaging for Physical and Biological Sciences (I and II)

The discovery and interpretation of X-ray diffraction from crystals by von Laue, Henry and Lawrence Bragg about a century ago marked the beginning of a new era for visualizing the three-dimensional (3D) atomic structures in crystals. In 1999, the methodology of X-ray crystallography was extended to allow the structure determination of non-crystalline specimens, which is known as coherent diffractive imaging (CDI) or lensless imaging. In CDI, the diffraction pattern of a non-crystalline sample or a nanocrystal is first measured and then directly phased to obtain an image. The well-known phase problem is solved by combining the oversampling method with iterative algorithms. In this talk, I will present the principle of CDI and illustrate its broad applications in physics, chemistry, materials science, nanoscience, geology and biology using synchrotron radiation and X-ray free electron lasers.

Cinzia Giannini
Italy
National Research Council – CNR
Institute of Crystallography – IC

Lecture:
X-ray Diffraction and Imaging of Smart Nanomaterials

Smartness is a typical feature of biological systems that are able to adaptively interact with the environment. Indeed, more or less complex biological systems are able to modify themselves on the basis of the information they get from the surrounding environment in order to respond to such stimuli. Similarly, the term “Smart” generally refers to those materials that, in response to a deliberately imposed external stimulus or to changes in their surrounding conditions, are able to reversibly modify one or more of their functional or structural properties. The external stimuli causing the smart response of the materials could be of various kinds: physical (temperature, light, electric or magnetic fields, etc.), chemical (pH, analyte concentrations in air, water, biological fluids), and mechanical (stress, strain). It is intended that the process is fully reversible: a Smart Material is capable of returning to its initial state as soon as the trigger (external stimulus) is removed.

Widely known examples of Smart NanoMaterials include:

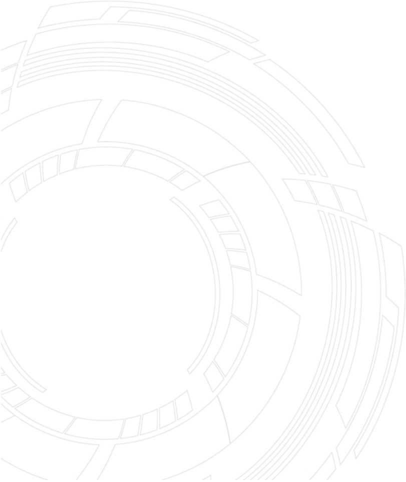
- Healthcare: nanoparticle suspensions or solutions to be injected into living tissues to help diagnostics or drug delivery;
- Energy: large-scale nanostructured materials/devices, thanks to their high surface to volume ratio, are potentially superior triggers to enhance every type of surface- or interface-based chemical reaction, i.e., reactions for energy generation, conversion and storage;
- Automotive/infrastructure: composite materials (ex: polymers) containing nano-objects with extraordinary mechanical properties can result in novel outstanding performances, enabling for instance the application of novel coatings with unprecedented resistances.

The synthesis of nanomaterials is indeed a main research field of nanotechnology. Presently, a variety of physical and chemical methods are used to grow or fabricate nanomaterials of different chemistry, size and shape.

To exploit the full potential that smart nanomaterials offer, a non-destructive structural and morphological characterisation is required.

Nanomaterials could be dispersed in solutions (such as nanocrystals, liposomes, hydrogels for biomedical applications), embedded in different matrixes (nanomaterials in polymers) or deposited on top of surfaces or underneath them (nanostructured organic field effect transistors).

In this lesson few relevant examples of structural/morphological characterization of colloidal nanocrystals with X-ray diffraction and X-ray imaging techniques will be given. Case studies of noble metal nanocrystals, hybrid nanocrystals, periodically assembled nanocrystals, nanocrystals in solution and non-periodically assembled nanocrystals will be shown, specifying - when needed - if a focused but partially coherent nano/micro X-ray beam should be adopted, or alternatively when coherent X-rays are mandatory.



Ercan Alp
USA
Argonne National Laboratory
Advanced Photon Source

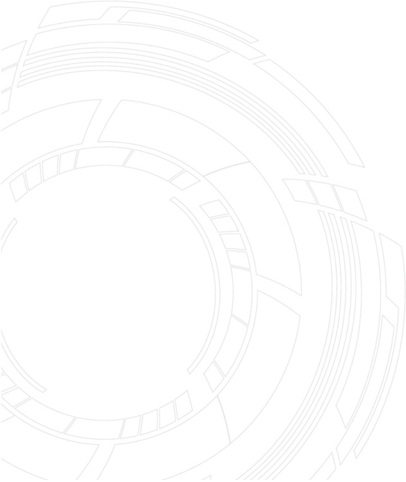
Lectures:
Inelastic X-Ray Scattering - Principles and Applications (I and II)

Daniela Zanchet
Brazil
Universidade Estadual de Campinas – Unicamp
Instituto de Química

Lecture:
X-ray scattering and absorption in Catalysis

Eduardo Granado
Brazil
Universidade Estadual de Campinas – Unicamp
Instituto de Física Gleb Wataghin

Lecture:
Novel magnetic and superconducting materials investigated by x-ray diffraction and spectroscopy at LNLS



Narcizo Marques
Brazil
Centro Nacional de Pesquisa em Energia e Materiais – CNPEM
Laboratório Nacional de Luz Síncrotron – LNLS

Lecture:
Rare-earths under high pressure

Mario T. Murakami
Brazil
Brazilian Biosciences National Laboratory – LNBio

Lecture:
Structural Biology

Julio Criginski Cezar
Brazil
Centro Nacional de Pesquisa em Energia e Materiais – CNPEM
Laboratório Nacional de Luz Síncrotron – LNLS

Lecture:
Soft X-Ray Spectroscopy at LNLS

Andrea Dessen
France
Centre National de la Recherche Scientifique – CNRS
Institut de Biologie Structurale J.P. Ebel

Lectures:
Synchrotron data collection and analysis of biological macromolecules (I and II)

Maria Carmen Asensio
France
Soleil Synchrotron

Lectures:
Angle Resolved Photo Emission Spectroscopy, ARPES (I and II)

This course will cover a wide range of topics around the electronic and chemical structure determination using angle resolved photoelectron spectroscopy (ARPES) of homogeneous, micro- and nano-structured materials. The class will start with an overview of major measurement tools as well as their history followed by a discussion on fundamentals, concepts and definitions. Although photoemission principles have been known for many decades, the most recent enthusiasm in this field has been renewed by remarkable instrumental developments and demanding advances materials. This course will include a review of those remarkable evolutions and strategic studies.A significant amount of time will be devoted to most recent progresses in imaging via k-space ARPES, which provides detailed k-versus-energy characterization and identification, with micro- and nano-scale spatial information over large areas within minutes. Basic design parameters of these state-of-the-art instruments will be summarized and reviewed. In the last part of the course, an overview of the potential applications for homogeneous, pattered and nano-objects materials in the field of metals, semiconductors and oxides will be provided. Typical examples will be given and challenges in technology adoption will be discussed. The course will conclude with a conversation on the remaining design and manufacturing issues as well as an outlook for the strategy of measuring electronic structure using a multi-scale approach.This course is targeted for a very broad audience, from materials, life science, nanotechnology scientists and engineers to researchers in both academic and industry who are engaging research and developmental work based on chemical and electronic structure of materials.

1. J. Avila and M.C. Asensio, Synchrotron Radiation News, 2014, 27(2): 24-30
2. J. Avila et al., Sci. Rep. 3 (2013) 2438, DOI: 10.1038/srep02439
3. L. I. Johansson et al., Sci. Rep. 4 (2014) 4157, DOI: 10.1038/srep041
4. L. Brown et al. Nano Letters, 2014, 14 (10): 5706–5711
5. G. Lippert et al. Carbon, 2014, 75: 104-112
6. H. Coy Diaz et al. Nano Letters, 2015, (15): 1135–1140

Ruben Reininger
USA
Advanced Photon Source (APS) – Argonne National Laboratory

Lectures:
X-Ray Optics simulations and current developments on software packages (I and II)

Daniel Haskel
USA
Argonne National Laboratory
Advanced Photon Source – APS

Lectures:
Magnetism/high pressure with X-rays (I and II)

Donald Sparks
USA
University of Delaware
College of Agriculture & Natural Resources

Lectures:
X-Rays in Soil Science (I and II)

Simo Huotari
Finland
Division of Materials Science – Department of Physics
University of Helsinki

Lecture:
X-Ray Raman Spectroscopy and Imaging (I and II)

Ryan V. Tappero
USA
Brookhaven National Laboratory
National Synchrotron Light Source – NSLS

Lectures:
Introduction to Techniques and Environmental Science Applications of Synchrotron X-ray Fluorescence Microprobes (I and II)

Environmental studies often require characterization of elemental abundances and speciation in samples that are heterogeneous at the micrometer and sub-micrometer scale. Synchrotron radiation sources are ideal for developing high intensity, highly-focused X-ray probes for characterizing the speciation, transport and reactions of trace elements in biotic and abiotic components with detection sensitivities in the attogram range and spatial resolutions less than 1 micrometer. This presentation gives an overview of new developments and trends in how these instruments are being used to address environmental problems.

Synchrotron radiation sources are ideal for developing high intensity, highly-focused X-ray probes for characterizing the speciation, transport and reactions of trace elements in biotic and abiotic components. In particular, micro-XRF allows one to image and quantify the distribution of trace elements in samples with detection sensitivities at the attogram level. Micro-XAS analysis allows one to quantify oxidation state ratios in heterogeneous earth and biological materials at spatial resolutions less than 1 micrometer. Coupled X-ray-fluorescence, -spectroscopy and -diffraction analysis allows one to quantify the abundance and speciation of elements at trace concentrations and evaluate the mineralogy to which they are adsorbed or bound. Such information is crucial in understanding the toxicity, mobility and containment of toxic metals in the environment, mechanisms of trace element partitioning, and paths of strategic metal enrichment in nature.

Synchrotron-based micro-analytical techniques offer distinct advantages over other analytical techniques by allowing analyses in situ, an important example being the ability to determine chemical speciation of a wide variety of toxic elements in moist soils, waste-forms, and biological specimens with little or no chemical pretreatment at detection limits that typically exceed those of conventional methods by several orders-of-magnitude. New fast scanning detectors and amplifiers are allowing many beamlines to image relatively large samples with minimal overhead. Often these measurements can be done as tomographic analyses, allowing three-dimensional rendering of trace metal distributions in samples without the need for physical sectioning.

Scanning X-ray microprobes are typically optimized for imaging or spectroscopy. Instruments with the highest spatial resolutions typically rely on diffractive optics (e.g., zone plates) for focusing, whereas instruments designed for high-quality spectroscopy measurements typically rely on reflective optics such as Kirkpatrick-Baez (KB) microfocusing mirrors; KB mirrors have the advantages of achromaticity (all energies are focused to the same spot), achievable gains in flux density in excess of 104, and long working distances (centimeters) to accommodate an array of ancillary instruments (custom environmental cells, etc.). Recent improvements in mirror flatness, bender designs, and nested mirror geometries have allowed these devices to routinely achieve spatial resolutions of a few hundred nanometers. Coupled with the smaller beam emittance provided by newer synchrotron facilities, next generation KB-mirror-based probes can achieve spatial resolutions below 50 nm, making it feasible to optimize for both imaging and spectroscopy. Introductory examples will be given of how users of these instruments are applying these techniques.

Dalton Abdala
Brazil
Centro Nacional de Pesquisa em Energia e Materiais – CNPEM
Laboratório Nacional de Luz Síncrotron – LNLS

Lecture:
X-ray spectroscopy in soils

São Paulo School of Advanced Sciences on

Recent Developments in Synchrotron Radiation

July 13th - 24th, 2015, Campinas, Brazil

ABSTRACTS

Plasmonic influence on reactivity of gold based - supported nanoclusters

Antoine Abisset[1], Yvonne Soldo[1], Aude Bailly[1] and Marie-Claire Saint-Lager[1]

[1] *Institut Néel, Département MCMF, 25 rue des Martyrs BP 166, Grenoble, France*
antoine.abisset@neel.cnrs.fr

Recent experiments [1,2] have shown an important increase of the catalytic activity for chemically synthesized gold nanoparticles under visible light exposition. Such phenomenon, attributed to surface plasmon on nanoparticles (SPN) modes, is particularly relevant in the context of energy-efficient processes using solar light.

A mandatory step for further developements is to have a great comprehension of these SPN-assisted processes, especially at the nano/atomic level. We aim to study model systems [3], namely gold-based nanoclusters deposited on TiO2, exploring the link between the catalytic activity and the plasmonic properties, with coupled and in situ (during the reaction) surface science techniques.

I will present the activities of my team, emphasizing on my thesis topic.

[1] Sarina et al., JACS 135 (2013).
[2] Mukerjee et al. Nano Lett 13(2013).
[3] Laoufi J. Phys. Chem. C 115 (2011).

Photoemission Electron Microscopy Branch of SpectroMicroscopy beamline of the Iranian Light Source Facility

Somayeh Amiri[1], A. Gholampour Azhir[1] and M. Lamehi Rashti[1]

[1] *Iranian Light Source Facility (ILSF), Institute for Research in Fundamental Sciences, Tehran, Iran - Amirisomayeh@ipm.ir*

Spectromicroscopy (SM) beamline is one of the most priorities in ILSF day-one beamlines due to its wide range of applications and big potential user community in Iran. It will be devoted to the photoemission spectroscopy techniques and will have two end stations in two independent branches: one for Photoemission Electron Microscopy (PEEM) measurements and the other for scanning photoemission microscopy (SPEM) [1]. In this study, PEEM branch design has been considered. The beamline is designed to cover the 90-1500 eV energy range with about 0.6×10^4 resolving power, and the minimum spot size of about 10×4 μm^2 at sample position. Brilliance, flux distribution, power distribution and photon size and divergence in the whole range of energy has been calculated for a 1.6 m helical undulator with maximum undulator strength parameter $K_{max}=5$ using SPECTRA code [2]. The optical layout has been decided to be includes of a collimating mirror, a varied included-angle plane grating monochromator, and a KB bendable elliptical cylinder mirror. The ray tracing calculations done by SHADOW and RAY [3,4], gives us the most important parameters of the photon beam in different part of the beamline. Two plane gratings with different uniform line density (700, 900 lines/mm) have been used to cover the whole energy range with the resolving power of $0.4\text{-}0.6\times10^4$ depending on the photon energy.

[1] J. Rahighi et al, International Particle Accelerator Conference, China, (IPAC13) p. 1137, 2013.
[2] http://radiant.harima.riken.go.jp/spectra
[3] www.esrf.eu/usersandscience/experiments/TBSscisoft/xop2.3
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New Design of Powder Diffraction Beamline of ILSF With the Wiggler Source

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X-ray Powder Diffraction beamline is one of the first priorities of the Iranian Light Source Facility (ILSF) day-one beamlines [1]. This beamline will cover the research requirements of the scientific community in the fields of physics, material science, chemistry etc. Preliminary design and ray-tracing of the powder diffraction beamline of ILSF has been performed [2]. Parameters of the proposed wiggler magnet as a source of this beamline include λ=6 cm, K=7.05, E_c=7.5 keV, B_m=1.26 T, have been optimized and determined by SPECTRA code and analytical calculations [3, 4, 5]. Optical layout of the beamline is consist of collimating cylindrical mirror, sagittaly focusing Si (111) Double Crystal Monochromator (DCM) and meriodionally bent cylindrical mirror for the focusing photon beam at the sample. In this stage optical surface of the elements have assumed perfect and energy resolution of the beamline is almost 10^{-4} and flux at sample is between 10^{13} to 10^{14} ph/s/0.1% B.W. of DCM. Spot size at sample can be altered from 368×23 μm^2 to 10×1 mm^2 by changing radius of the focusing mirror and the curved crystal. Flux at sample and power through beamline have been calculated as well.

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In situ ptychography during the annealing treatment of heterogeneous nanoporous gold catalysts

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In order to understand structure-activity relationships in catalysis, microscopic studies under controlled environmental conditions (elevated temperature, gas flow, pressure) are needed at different length scales [1]. For imaging on the atomic scale, usually transmission electron microscopy (TEM) is used, but for the meso scale (50 nm to 1 µm) and for i*n situ* applications, the short penetration depth of electrons is limiting and X-rays are more suitable [2]. To obtain a high resolution in X-ray microscopy, a focused X-ray beam and special techniques like ptychography are required. Moreover, appropriate *in situ* cells need to be developed.
Here we show a newly developed *in situ* cell, which was used to study nanoporous gold (np-Au) based catalysts. Np-Au has received strong attention for heterogeneous catalysis and has been modified to be suitable for different reactions such as CO oxidation or water gas shift reaction [3] by supporting metal oxide particles on the np-Au surface. This is crucial for the catalytic activity and prevents coarsening of the gold nanostructure at high temperatures, which enables high temperature applications. In order to achieve sufficient resolution, ptychography [4] was used to study the coarsening of np-Au at the nm scale.

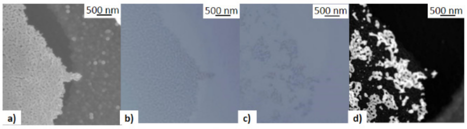

Figure 1: a) SEM image (vacuum) of np-Au before annealing, b) ptychographic reconstruction (phase contrast) before annealing inside the *in situ* cell, c) ptychographic reconstruction (phase contrast) during annealing at 350°C inside the *in situ* cell, d) TEM image (vacuum) after annealing.

Results on *in situ* ptychography during annealing in a flow of synthetic air will be presented as well as the setup used for the *in situ* measurements. The cell is based on a sample holder composed of a TEM heating chip and a cell body with X-ray transparent windows. The sample can be kept under a controlled atmosphere while heating and the chip can be used for electron microscopy as well. Figure 1 shows a comparison of a SEM (scanning electron microscopy) image, ptychogramms and a TEM image which present the same area of the sample. Complementary to the SEM and TEM measurements, the ptychography scans were taken *in situ* under a controlled gas flow at 10^5 Pa and at elevated temperature.
The results confirm the possibility of the new developed *in situ* cell to use the same chip for X-ray imaging and for electron microscopy. Therefore, different length scales (the atomic scale in TEM with restriction to reduced pressure, and the meso scale in X-ray microscopy with the advantages of *in situ* conditions) can be studied at the same area of the sample. This complementary information will help to understand structure-activity relationships and thus help to improve catalyst development.

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Anomalous X-Ray Diffraction Study of Pr-substituted $BaCeO_{3-\delta}$

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The effect of Pr doping on the crystal structure and site occupancy was studied for the nominally synthesized $BaCe_{1-x}Pr_xO_{3-\delta}$ (x = 0, 0.2, 0.4, 0.6 and 0.8) perovskites using anomalous X-ray powder diffraction data and Rietveld analysis. Crystal structure parameters were accurately determined by using 10000 eV photons, and the Pr occupancy was refined using data collected with 5962 eV photons, close to Pr L_{III} absorption edge. $BaCe_{1-x}Pr_xO_{3-\delta}$ crystallizes in the *Pnma* (N° 62) Space Group for all x values [1]. Pr cations are mainly located at the Ce-sites (perovskites B site), but a small fraction of them increasingly substitute some of the Ba ions at the A site as Pr content increases [2]. The Pr doping introduces electronic defects (Pr^{+3}/Pr^{+4}) and oxygen vacancies needed for H_2O incorporation and H-ionic conductivity. The decrease of the orthorhombic distortion would produce opposite effects on the electronic and ionic mobility [3]. The electronic mobility should increase due to an improvement in the overlap of the (Ce/Pr)4f-O2p orbital, while the proton mobility should decrease as a consequence of a larger hopping distance [4].

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New results in the fundamental theory of synchrotron radiation

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For scalar and spin one half particles we consider the evolution of maximum in the radiation spectrum. A well-known approximation obtained for critical frequency in the framework of classical theory can not be applied when quantum corrections become significant. But there appears a possibility to find the conditions for the maximum to shift to the highest harmonic of finite quantum spectrum. We start with the simplest example where the spectral properties can be distinguished, namely, a quantum three-level system. In this case we find the parameters of radiation at which the second harmonic becomes dominant. Switching to the general case, we have shown that the shifts occur successively starting with primary harmonic in non-relativistic region, and this result remains valid independently of spin. For a scalar particle there exists a fixed set of numbers, which are the critical values of the magnetic field, such that the shift of radiation maximum in the spectrum of boson can only happen when the intensity of the magnetic field is greater than certain critical value related to corresponding harmonic. If this condition is not satisfied, the position of maximum remains unchanged. It turns out that the presence of spin perturbs this picture, so that the critical values of field intensity depend on the number of initial level. The accounting of the spin leads to a dramatic similarity between the classical predictions and the obtained quantum approximation.

Electron and Photon Impact Laboratory - UFRJ

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Our Laboratory has a long research tradition in the use of fast electrons and synchrotron radiation to excite and ionize molecules.
The major lines of research (1-6) have been:

- Photofragmentation of biomolecules containing the disulfide (S-S) chemical bond;
- Core excitation and ionic dissociation of natural products;
- Chemical characterization of the radiation damage induced in biomolecules by ionizing radiation (fast electrons and synchrotron radiation, S.R.).

Additional line of research currently under development:

- Elemental characterization and chemical speciation of Amazonian plants and human hair using ion beam and S.R.: XRF, NEXAFS and RBS.

We have scientific collaborations with groups from Brazil (Instituto Nacional de Pesquisas da Amazônia, IMPA and Instituto de Física da UFRJ) and from abroad (Departamento de Fisica, Universidade Nova de Lisboa, Portugal and Soleil,France).
Main available instumentation: an Electron Beam Irradiation Spectrometer, a Time-of-Flight Mass Spectrometer and a Wave-length Dispersed X-Ray Spectrometer (Bruker S8 Tiger 1 kW).

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Microbial Carbonates of Teresina Formation, Passa Dois Group, Paraná Basin, Brazil

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Teresina Formation (Permian, Paraná Basin, Brazil) represents the transition from the marine environments to a marine zones with shallow water influenced by storms. This formation presents, in its intermediate portion, limestone and oolitic limestones, in which we can observe flaser structures, wavy laminations, ripples and microbial mats. We have studied three carbonate levels located in one outcrop at Taguaí city, state of São Paulo, which consists of microbial mats with ooids and oncoids. The objective of this study was to characterize these carbonates, understand the relationship of metazoan living in association with these microbial mats, and to provide additional information for the depositional history of this formation. We perform analysis of thin sections, SEM/EDS and Raman Spectroscopy, as well as field studies. The main results were that among bioclasts found inside microbial mats, there were ostracods shells and peloids (these perhaps associated with the preservation of microorganism colonies, or indicating an intense activity of detritivorous organisms that fed the microbial mats). The compositional analysis results show hematite and barite minerals possibly of microbial origin. Raman spectroscopy mapping allowed the delimitation of areas with oncoids showing cores formed by quartz and ostracods shells with calcite or aragonite cortex, being the latter an indicator of freshwater influence. The main conclusions were that, since the Permian basin had lost the connection to Panthalassa ocean, the streams were originated from rainfalls which caused a decrease on salinity levels in the system, that influenced the development of microbial carbonates. In dry periods, microbial mats resected and formed structures that resemble mudcracks. These informations, added with rock analysis corroborate the hypothesis of dry and sporadic rain cycles, associated with the process of continentalization of the Paraná Basin which resulted paleogeographic changes.

Characterization of nanocatalysts for ethanol production from CO hydrogenation with Synchrotron-based techniques

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Energy demand has caused an increase of petroleum-based fuels consumption. Petroleum-based fuels carry several disadvantages like greenhouse gas emissions, limited sources, and high cost.[1, 2] As a consequence, it is necessary to develop alternative energy feedstocks like biofuels. Ethanol is a promising alternative due to its ease of production, high energy density, low toxicity and compatibility with the existing infrastructure. Bio-ethanol is produced through biomass fermentation, however, these processes are relatively inefficient and difficult to scale to meet global energy demands. Heterogeneous catalysis is the mainstay of large scale feedstock production, and processes such as direct syngas conversion (mixtures of CO, CO_2, and H_2) to alcohols is thermodynamically favorable and scalable, but progress has been slowed by the need for more efficient and selective catalysts. Direct ethanol synthesis from syngas is a complex reaction pathway that involves the hydrogenation of CO and CO_2.[3, 4] Side reactions that impact ethanol yield and selectivity are methanation and the water gas shift reaction. To overcome these challenges, metallic catalysts have been widely studied under CO hydrogenation conditions. The best performing and most selective for ethanol are rhodium-based nanocatalysts.[5] Rhodium can increase C_2^+ oxygenate and ethanol selectivity due its ability to form C-C bonds but with high undesirable methane yields.[6] The performance of Rh-based catalysts can be improved by the use of a metal promoter or modification of support. Common promoters are transitions metals that aid CO dissociation and insertion while suppressing the hydrogenation of $(CH_x)_{ad}$ intermediates.[7] The support's advantages is their electron withdrawing/donating capability, change of morphology of the metal, and effect of support on the reducibility of the metal.[8] In order to develop a highly efficient and selective nanocatalyst for ethanol synthesis, it is essential to understand the diverse interactions amongst the diverse components of the catalyst. Synchrotron sources provide high intensity x-rays, which are important for probing the chemical environment of our catalysts materials that have low metal concentrations and small particle sizes. Furthermore, in-situ studies are needed to trace the evolution of the atomic and electronic structure of the catalysts under reaction conditions, which is attainable due to the ability of synchrotron x-rays to penetrate reactor cells at high pressures. Two techniques are performed to probe the local and average atomic structure and electronic state of the atoms on the nanocatalysts: x-ray diffraction (XRD) and x-ray absorption spectroscopy (XAS). The structural and electronic information obtained can ultimate help us design a highly efficient and selective Rh-based nanocatalyst for ethanol synthesis from CO hydrogenation.

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Micro-PIXE Mapping of Elemental Distribution in Roots of a Mediterranean-type Sclerophyll, *Agathosma betulina* (Berg.) Pillans, Colonized by *Cryptococcus laurentii*

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Most plants growing in Mediterranean-type ecosystems characterized by low nutrient soils increase host nutrition by forming mutualistic associations with microsymbionts such as mycorrhizal fungi and *Rhizobium*. However, little is known about the role rhizosphere yeasts may play as nutrient-scavenging microsymbionts in nutrient-impoverished Mediterranean-type heathlands. The aim of this study was to assess the effect of a basidiomycetous soil yeast, *Cryptococcus laurentii*, on the nutrition of *Agathosma betulina* (Berg.) Pillans, a slow-growing perennial sclerophyll recognized for its ethno-botanical and medicinal value. Seedlings of *A. betulina* were either inoculated with an isolate of *C. laurentii* obtained from the rhizosphere of wild *A.betulina* or with autoclaved yeast (controls) and grown under low nutrient conditions. Harvested roots of both treatments were analyzed using micro-proton-induced X-ray emission spectrometry to quantitatively assess elemental distribution within root tissues. To aid in the interpretation of heterogeneous elemental distribution patterns, fluorescence microscopy was used to detect apoplastic barriers (Casparian bands) in roots of both treatments. Light and transmission electron microscopy was also used to detect endophytic yeast in root cross-sections of yeast-inoculated and control plants. Roots of yeast-inoculated plants had significantly ($P < 0.05$) higher average concentrations of P, Fe, and Mn, compared to control roots. No endophytic yeast were detected and elemental enrichment in the epi/exodermal-outer cortical tissues was correlated with the presence of Casparian bands in the exodermal cells. This symbiosis is likely to have a significant ecophysiological impact on plant fitness that would allow survival in the absence of mycorrhizal fungi in Mediterranean-type ecosystems.

Comparative Biophysical Characterization of Heterotrimeric G-protein Alpha (α) Subunit (AtGPA1) in *Arabidopsis thaliana*

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The heterotrimeric guanine nucleotide-binding proteins (G-proteins) mediate the transmission of signals from G protein coupled receptors (GPCR) to effector systems such as ion channels, enzymes and intracellular second messengers in several organisms including yeast, mammals and plants. The heterotrimeric complex is comprised of the alpha (Gα), beta (Gβ) and gamma (Gγ) subunits; Gα has GTP binding and hydrolysis activity, and Gβ and Gγ interact with downstream effectors as a dimeric complex. Although the complete structure and activation mechanism for the mammalian complex are known in detail, these are still controversial for plants. Plant heterotrimeric G-proteins have been shown to be involved in multiple physiological processes, such as regulation during development of leaf shape, cell proliferation, lateral root formation, stomatal density as well as control of the post germination process. In order to elucidate the activation mechanism in plants and for a better understanding of the G-protein-mediated molecular pathways, a structural investigation of the *Arabidopsis thaliana* complex has been undertaken.

In this study, biochemical characterization of the full length wild type (WT) and a mutated (N-terminal-36 aa truncated) version of A.thaliana G alpha subunit (AtGPA1) is presented. WT GPA1 had been cloned in *Pichia pastoris* [1] and recently the mutated version of GPA1 is produced in *E.coli*. Both recombinant proteins are purified and nucleotide (GTP, GDP, GTPγS) binding is determined by absorbance spectroscopy to show their likeness to the "native" state. Their level of oligomerization is studied by Dynamic Light Scattering (DLS) and the secondary structure elements are determined by Circular Dichroism Spectropolarimetry (CD). Parallel to comparative biochemical characterization and biophysical characterization studies such as DLS and CD analysis, Small Angle X-ray Scattering (SAXS) will be used to investigate differences in molecular shape. Results of these studies will be presented in the framework of a structural comparison of the WT and the truncated GPA1 proteins.

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Microstructural and physical characterization of Co-based superalloy

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In this work was focused on to understand Nb adding effects in the composition, the phase transformation reaction temperatures and the phase equilibria of Co-based superalloys. The Nb adding in Ni-based superalloys facilitate the precipitation of carbide, gamma prime and gamma double prime precipitates. In this way, it was evaluated if the Nb perfoms the same function in Co-based superalloys. The Co alloy was produced by arc melting furnace in this composition (%at.) 40Ni-10Cr-10Al-7.5W-0.6C-0.06B-3(Nb,Ta). To identify the two alloys it was named Co-40Ni-3Ta alloy with Ta adding and Co-40Ni-3Nb alloy with Nb adding. The characterization of microstructural featuring encountered in these two alloys were carrying out using FEGSEM and XRD. Chemical composition of phases was measured using XEDS and XRD from bulk was made to identify crystalline phases. In Co-40Ni-3Ta and Co-40Ni-3Nb the matrix phase was by γ-Co dendrite and γ′-$Co_3(Al,W)$ having spheroidal morphology in it. The big difference was identified in the interdendritic region. For Co-40Ni-3Ta was encountered only the Laves/γ eutectic structure with Laves having $MgNi_2$ structure. For Co-40Ni-3Nb was found the MC/γ eutectic with script-like morphology, plates from Co_7W_6/Laves($MgNi_2$ strucuture) phase and CoAl/γ′-coarsen precipitates surrounding these plates. In XRD results peaks from these phases was indexed in diffratogram but due to texturing macrostructure formed from cooling conditions during arc melting processes of alloys it turns hard to quantify phase fraction of these phases present in alloys. Qualitatively the results of SEM and XRD showed good agreement.

<table>
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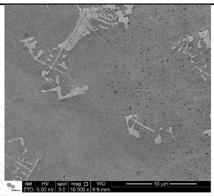
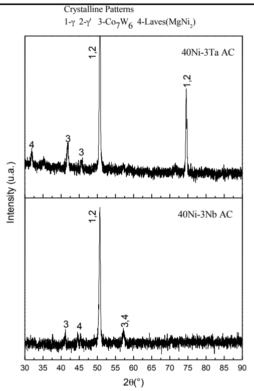
<tr><td>

Co-40Ni-3Ta</td><td rowspan="2">
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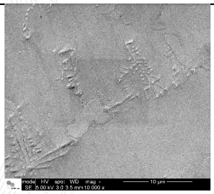
<tr><td>

Co-40Ni-3Nb</td></tr>
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Preparation and Characterization of Modified Crystals of Nevirapine

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The antiretroviral drug Nevirapine (NVP) (11-Cyclo-propyl-5,11-dihydro-4-methyl-6H-dipyrido[3,2-b:2',3'-e][1,4]diazepin-6-one) is a non-nucleoside reverse transcriptase inhibitor used in the treatment of HIV-1 infection. According to the Biopharmaceutics Classification System (BSC)[1], it is a class II drug, exhibiting low solubility and high permeability. In order to increase the drug dissolution and its bioavailability, different preparation methods to modify the crystal structure have been studied[2,3,4]. This new crystal forms can be solvates, hydrates, co-crystals and/or polymorphs. In this work, some preparation methods have been adopted and there is a special interest in co-crystals formation.

Co-crystals are multicomponent solids that can be polymorphs. In its structure there are different drug molecules or a drug and a non-volatile substance[5]. NVP molecule has a conformationally rigid amide group that allows a co-crystal formation with soluble carboxylic acids or amide co-formers[2]. The goal is to develop and evaluate a scalable preparation method to obtain pure forms of co-crystals of NVP.

Five co-formers have been tested: saccharin (SAC), salicylic acid (AS), caffeine (CAF), urea (URE) and theophylline (TEO). Two methods have been evaluated in co-crystal preparation: 1) physical mixture of NVP and co-former with heating and 2) slurry milling process, with different stoichiometries and solvents. The physical-chemical properties of the materials have been characterized by different methods, such as X-ray diffraction (XRD), scanning electronic microscopy (SEM), differential scanning calorimetry (DSC) and solid state ^{13}C NRM.

The fact of these materials could produce diffraction patterns with some identification problems, such as preferential orientation, and in order to improve the identification and characterization of the solid phases, it is necessary use the síncrotron radiation and XDR beamlines in some cases.

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UVA-Induced Damage To Dna Studied By Means Of X-Ray Absorption Spectroscopy

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Epidemiological and molecular evidence suggests that DNA damage generated by sunlight is one of the most important factors in the skin cancer etiology [1]. Sunlight consists of three types of ultraviolet radiation: UVA (315–400 nm), UVB (280–315 nm) and UVC (<280 nm) with UVA being the predominant component. Nevertheless, the molecular mechanisms that underlie various forms of radiation-induced DNA damage are still unclear. Especially the role of direct and indirect effects in UVA-induced damage is the subject of extensive studies. The absorbance of UVA light by DNA, although believed to be small, is not insignificant. It was also shown that UVA can produce oxidative free radicals [2]. This can lead to a number of lesions such as breaks in the phosphodiester backbone [3], which is one of the most dangerous types of cellular damage, or the formation of cyclobutane pyrimidine dimer (CPD) [4]. All of these lesions result in a distortion around the phosphorus atom in the DNA phosphodiester backbone.

In the presented studies we used X-ray absorption spectroscopy (XAS) to investigate the molecular structure of the damage caused by UVA irradiation. As a model of DNA molecule we used calf thymus DNA (Sigma-Aldrich), which was irradiated by UVA in dry form and in aqueous solution. This allowed us to compare the influence of sample environment on radiation effects. Non-irradiated sample was used as a reference. XAS measurements were performed at the phosphorus K-edge to investigate how the local structure around the P atom in DNA molecule is affected by UVA radiation damage. The experiment showed an increase in the white-line intensity between the spectra of damaged DNA compared to the reference sample. The largest difference between spectra was observed in case of DNA irradiated in aqueous solution while the spectra of DNA irradiated in dry form with the same radiation source and conditions showed negligible difference. The experimental results are compared with theoretical calculations performed with FDMNES [5] code in order to identify the ratios and structure of each damage type caused by UVA.

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Heterojunctions of Graphene/Nanoparticles: a GISAXS Characterization

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Graphene (G) was the first two-dimentional (2D) crystalline material isolated and characterized. This new nanocarbon exhibited unusual and unique chemical and electronic properties compared to its counterpart, graphite.[1] This fascinating discovery was aworded in 2010 with a Novel Prize in Physics honoured to A. Geim and K. Novoselov. Since then, the scientific community is actively working in the development of different types of 2D structures that can mimic graphene´s attributes. Heterojunctions formed by a combination of G with metal nanoparticles (NPs) are a new class of nanomaterials that can be used in chemical/biological sensing,[2] catalysis, optoelectronics,[3] and surface-enhanced Raman scattering (SERS)[4] applications for just to mention a few. However, the structure and conformation of these heterojuntions should be explored more in detail in order to develop future applications.[5] In this work we chemically synthesized alkylamine- and alkylthiol-coated Au nanoparticles (NPs) and assemble them as films on graphene and silicon substrates. We perform Grazing-incidence small-angle X-ray scattering (GISAXS) experiments in order to monitor the NPs assembly (i.e: order and structure), internanoparticle distance, and thermal stability of these films. We also explore the use of dithiol molecules in order to improve NPs correlation and control the internanoparticle distance. Interesting preliminary results showed that graphene (substrate) and dithiol linkers provide correlation to those NPs. The increase in temperature during thermal treatment leads to the loss of NPs correlation likely caused by NPs annealing and film colapsing.

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Amyloid Fibres Formed from the Self-Assembly of an Arginine/Phenylalanine Oligopeptide*

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Peptide fibrillization is a relevant topic often associated to neurodegenerative disorders such as Alzheimer's, Parkinson's and Huntington's diseases. Understanding the mechanisms involved in the aggregation process is an important step toward the development of strategies for control and treatment. In this work, a model sequence composed exclusively of arginine and phenylalanine, the octapeptide RFRFRFRF (RF8), has been synthesized and its fibrillization, investigated. The self- assembly was evaluated and many features of amyloid-like analogs such as the canonical cross-_structure and the formation of intermediate aggregates during the fibrillization pathway have been identified. Particularly, the structure of these species has been investigated in detail through the combination of highly-resolved fibre XRD and *in situ* analysis using small-angle X-ray scattering. The findings presented here are the first detailed report on the self-assembly and structure of amyloid-like analogs from binary simplified oligopeptides based on arginine moieties. Fluorescence and UV-Vis assays were used to determine critical aggregation concentrations, corresponding to the formation of oligomeric species and _-sheet rich structures organized into both spheroidal aggregates and highly-ordered fibrils. TEM and AFM images showed globular aggregates and long unbranched fibres with diameters ranging from ~ 4 nm up to ~ 40 nm. FTIR and circular dichroism spectroscopy confirm the presence of β-sheet structures and X-ray fibre diffraction on oriented stalks provides detailed information on the structure of the fibres indicating peptide organized into layers based on an orthorhombic unit cell. *In situ* small-angle scattering (SAXS) shows the presence of low molecular weight oligomers in equilibrium with mature fibres which are likely made up from 5 or 6 intertwined proto-filaments. Our results show that the RF8 octapeptide is a useful model peptide, with a highly simplified sequence, incorporating dual functionality from aromatic and cationic residues, that forms amyloid-type _-sheet rich fibrils and other amyloid-like analogs along its self-assembly pathway.

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Development of a TBC system for use in F-type thermoelectric generation turbines

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Thermal Barrier Coating system (TBC) has a big role in the evolution of gas turbine engines, because their efficiency has increases with de improvement of their materials to resist at high temperatures. This system is composed of Top coat (TC) generally is used ZrO_2 –based having a composition containing 7 wt% Y_2O_3 (7YSZ); the Bond Coat (BC) is made with complex MCrAlY (M=Ni, Co+Ni, or Fe) alloy, the Thermally Grown Oxide (TGO) is a very thin film of alumina (Al_2O_3) generated by the thermal process in the barrier and, finally, the substrate is a Nickel based super alloy [1, 2]. This is a complex system that supports high temperatures, and wear; however, the components durability are not enough to the actual exigencies. The principal challenge is increase the operation temperature and reduce the excessive growth of the α-Al2O3 (TGO) results in the depletion of Al in the bond-coat. The Al depletion, results in the formation of other oxides, such as Ni- and Co-containing spinels, $Y_3Al_5O_{12}$, and Y_2O_3. The formation of these phases compromises the structural integrity of the TGO and accelerates localized oxidation by providing fast oxygen-diffusion paths [2].
On my first year of doctoral studies, the objective is understand the thermal phenomena and failures mechanisms of TBC system, to will propose a new TBC system, to increase operation temperature of the turbine and, reduce all the damage caused by thermal stress and formation of spinels.

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In situ study of oxide-supported gold nanoparticles by surface X-ray scattering techniques

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Gold nanoparticles have been extensively studied for their high catalytic activity in CO oxidation reaction. The preparation technique of the nanoparticles and the type of support has great impact on the catalytic behavior of the system. To effectively monitor the effect of size on CO oxidation, we study gold nanoparticles synthesized by micelle nanolithography, a technique well adapted to yield minimal size distribution of nanoparticles. Here, we synthesized 3nm and 15nm gold nanoparticles using the micelle nanolithography technique. To achieve monodisperse metal-loaded micelles on MgO (001) substrates we employ spin-coating and observe quasi-hexagonal ordered micelles in the SEM. Atomic oxygen and hydrogen were used to remove the polymer and reduce the gold ions and enable, nanoparticle formation. We made a systematic approach to study the effect of atomic hydrogen and oxygen during the formation of the nanoparticles by means of surface X-ray scattering techniques at SixS Beamline, Synchrotron SOLEIL, France. Grazing incidence X-ray diffraction (GIXRD) was used to determine the crystalline nature of the nanoparticles and their lattice constants. 3nm gold particles formed using atomic hydrogen, annealed at 700°C showed (111) epitaxy on MgO (001) substrate, which was not observed for the nanoparticles formed using atomic oxygen. In addition, x-ray reflectivity (XRR) and grazing incidence small angle x-ray scattering (GISAXS) techniques were used to complement the diffraction data. The activity of these nanoparticles towards the CO oxidation is under investigation using a flow reactor at SixS Beamline, Synchrotron SOLEIL.

Synthesis and Characterization of Single Site Heterogeneous Titanium Catalysts for Selective Oxidation

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Porous heterogeneous catalysts are of continuing interest in catalysis because of their easy separation from the reactants and products. A synthetic building block methodology has been developed for the preparation of single site, isolated, atomically dispersed metal based active sites within a silicate matrix. It is ideal to have one type of site to improve the activity and selectivity of the active site [1]. The synthetic approach uses a molecular precursor i.e. building block and the method of sequential additions to construct the matrix. This methodology can be used to target metal connectivities (2, 3, or 4 linkages) to the matrix in a tetrahedral geometry seen in Figure 1.

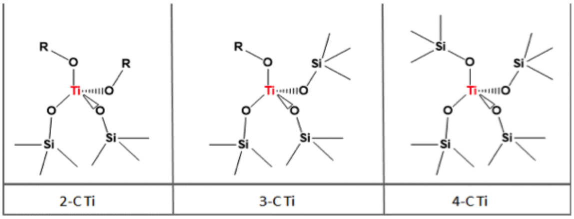
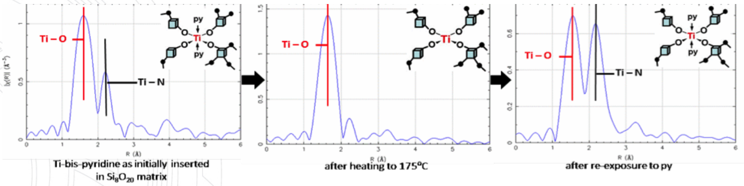


Figure 1: First generation titanium catalysts (2, 3, and 4 connected).

The primary focus of this research is to synthesize and characterize a second generation catalyst that will be a single site, atomically dispersed, titanium catalyst with a targeted connectivity to the silicate matrix, like the first generation, but will have altered geometries for a more accessible active site. Several characterization techniques are used to compare and contrast first and second generation catalysts; NMR, gravimetric analysis (determine connectivity), FTIR, XAS (XANES/EXAFS) (Figure 2), DRUV, and catalytic activity were used to characterize the final catalysts. XAS data was collected on beam line X19A at National Synchrotron Light Source at Brookhaven National Lab.



Ti-bis-pyridine as initially inserted in Si_8O_{20} matrix

after heating to 175ºC

after re-exposure to py

Figure 2: Preliminary EXAFS data showing the addition, removal, and re-addition of amine blocking ligands coordinated to titanium active site.

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Interaction of antitumor active dirhodium(II) carboxylates with thiol-containing biomolecules

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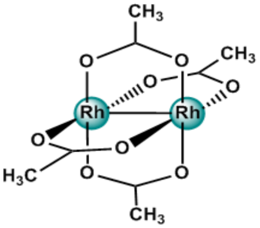

Figure 1 - ***Structure of dirrhodium(II) acetate***

Pioneering studies in the 1970s showed that dirhodium (II) carboxylate compounds with formula $Rh_2(RCO_2)_4$ (R= CH_3, CH_2CH_3, $CH_2CH_2CH_3$) (see figure below) exhibit remarkable anticancer activity towards different cancer cell lines, in some cases better than *cis*-platin [1,2]. Their mechanism of action is believed to be similar to that of *cis*-platin, with DNA as their main target [3] but in their way to DNA inside the cells, they can also target other biomolecules such as proteins, peptides and enzymes. So far, no structural information of the possible products of the reactions with sulfur-containing biomolecules have been reported.

Our studies are focused on the investigation of the reaction products of dirhodium (II) acetate, $Rh_2(CH_3CO_2)_4$, with amino acid *L*-cysteine and its derivatives (*D*-penicillamine and *N*-acetyl-cysteine), and glutathione, the most abundant thiol-containing peptide in cells. All information derived from this research will provide a deeper insight into the fate of such dirhodium (II) carboxylates in presence of thiol-containing biomolecules. X-ray Absorption Spectroscopy (XAS) has been helpful to define the local structure around the rhodium centres and their oxidation state. Rh K-edge EXAFS spectra in combination with other techniques such as ESI-MS and UV-Vis have led us to the conclusion that when such reactions are carried out in presence of air at physiological pH, the lantern structure of dirhodium (II) acetate (see image above) is broken down, the Rh^{II}-Rh^{II} bond is cleaved and the rhodium centers bridged by the ligand thiolate groups are oxidized to rhodium (III). Our experimental EXAFS and ESI-MS results, and structural information of the reactions products will be discussed.

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XMCD at Fe $L_{2,3}$ edges in three Fe-based precursors of Photomagnetic Prussian Blue Analogues

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The family of Prussian Blue and its analogues, referred as Prussian Blue analogues (PBA), exhibit thermal and photomagnetic bistability [1]. Nanoscale magnetic materials based on these interesting bistable properties are potential candidates for energy efficient, photoswitchable molecule-based information storage. In order to develop molecular nanomagnets with desired photomagnetic properties, the electronic and magnetic properties of the corresponding precursors must be investigated. In this talk, we present our results obtained on three Fe-bearing precursors (see figure 1) which are the building blocks of three photomagnetic FeCo Prussian Blue Analogues with cube [2], square [4] and linear dinuclear shape [5].

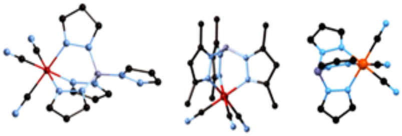

Fig.1 Molecular structures of the complex anions of three Fe(III) precursors **FepzTp** $[(\mathrm{pzTp})\mathrm{Fe}^{\mathrm{III}}(\mathrm{CN})_3]^-$ (left) [2], **FeTp*** $[(\mathrm{Tp}^*)\mathrm{Fe}^{\mathrm{III}}(\mathrm{CN})_3]^-$ (middle) [3] and **FeTp** $[(\mathrm{Tp})\mathrm{Fe}^{\mathrm{III}}(\mathrm{CN})_3]^-$ (right) [4]. Counter-cations, lattice solvents and hydrogen atoms are omitted for clarity. Color scheme: Iron – red, Carbon – black, Nitrogen – Light blue, and Boron – grey.

Element specific X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) measurements at Fe $L_{2,3}$ edges were performed on the DEIMOS beamline (SOLEIL, France). Ligand Field Multiplet (LFM) theoretical calculations combined with the experiment provided valuable information about the spin and orbit magnetic moments. For the three precursors, a very large value of orbital magnetic moment equal to $1.24\mu_B$ was obtained for Fe(III) ions as compared to the spin magnetic moment which is $0.98\mu_B$. The magneto-optical sum rules have also been applied to the calculated spectra to address the pertinent question of the applicability of the spin sum rule for $\mathrm{Fe}^{\mathrm{III}}$ (Low Spin) species.

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Cruzain Self-proteolysis Stabilization Leads to High Quality Crystal Structures

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The widely studied lysosomal cathepsins L, B, H, S, C and K, belong to the papain-like super family of cysteine proteases that are the most abundant and broadly distributed among living organisms. These proteins are expressed as inactive pro-enzymes that self-activate during the maturation event at slightly acidic pH, and become completely active for the hydrolysis of substrates at optimal pH values from 5.5 for Cat L to 6.8 for Cat H. [1,2] The acquisition of high-resolution crystallographic structures for these enzymes are challenging due the self-proteolysis that decrease the homogeneity of the protein solution during the crystallization process. Inhibitors that act by covalent irreversible mechanism exhibit high binding affinity and prevent self-proteolysis. In fact, most of the inhibitors reported at PDB for papain family of enzymes have this mechanism. However, the development of these inhibitors is currently avoided by pharmaceutical companies due the potential of off-target effects. Thus, in our current efforts on the discovery of new non-covalent reversible inhibitors we have to identify new ways to stabilize these cysteine proteases during the crystallization stage in order to provide the required structural information of the Mode of Binding (MOB). [1,2,3] Cruzain belongs to the papain-like family and is the major cysteine protease of the parasite *T.cruzi* being a validated therapeutic target to treat Chagas disease. [3,4] Herein, we show two crystal structures determined at high resolution of cruzain stabilized by Iodoacetamide (1.60 Å) and Methyl Methanesulfonate (1.95 Å). These small molecules bind covalently to the catalytic cysteine of all cysteine peptidases being irreversible in the case of iodoacetamide, and reversible in the case of MMTS. MMTS can be easily removed by reducing agents such as dithiothreitol (DTT). Crystals of cruzain inactivated by iodoacetamide or MMTS could be used for soaking with small inhibitors known as Fragments (that are also designed to probe interactions in different sub-sites of the enzyme), since until now there is no technology to get crystals of the Apo form of cruzain due the proteolysis. Cruzain was prepared as described by Lee *et al.* 2012 [4]. Crystals were equilibrated at 1.0 M LiCl, 0.1 M citric acid solution at pH 4.8 and for MMTS complex at 1.25 M $(NH_4)_2SO_4$ and 100 mM Hepes pH 7.5 using hanging drop method at 22°C. The crystal data were collected at ALS beamline 8.3.1 and the structures were solved and refined using Phenix package [5].

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Application of Synchrotron Based X-Ray Absorption Spectroscopy Techniques To The Geoscience Field

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X-ray absorption spectroscopy (XAS) is widely used at synchrotron radiation facilities and has been applied to solve numerous problems in soil science, mineralogy, and geochemistry worldwide. Unfortunately, this is not the case at the Brazilian Synchrotron Light Laboratory (LNLS), where the use of their facilities by geoscientists is very poor, not to say almost zero, according to their own statistics. From the side of the geoscientists, it is needless to say the amazing opportunities we are loosing by not taking advantage of such great facilities to solve complex environmental problems we face on a daily basis. By employing such powerful techniques to our complex problems we would be able to have a better knowledge about our systems. Not to mention that we would make the level of our work comparable to those currently done in the developed countries, where they already apply such techniques. From the side of LNLS, bringing a new set of users would increase the competitive edge and give the best possible use to the money invested by the Brazilian government in such a complex and expensive facility. The Department of Soil Science at Universidade Federal de Viçosa (UFV) and the LNLS are highly committed on increasing the number of geoscientists that are able to use synchrotron radiation. From the side of UFV we are very interested in learning and applying XAS techniques to our studies. On the other side, LNLS have been demonstrating a great interest in developing the geoscience field there. As mentioned above, the use of LNLS by geoscientists is nearly zero, a completely different picture from what is seen in other synchrotron light sources around the world. In order to give the best possible use to the money invested by the Brazilian government on its construction, maintenance, and development, LNLS needs to bring different users to increase the competitive edge of the proposals. The members from UFV have already had some type of involvement in projects where they applied or are going to apply XAS. The members from LNLS are experienced scientists with great knowledge on synchrotron-based techniques. From the members from UFV, with the assistance of Dr. Hesterberg, the visiting scientist of our project, they are expected to submit proposals to LNLS and to involve their students in order to turn themselves into LNLS users. The aims of this project are helping disclose and develop this incipient area of research in our country that is the application of XAS techniques to the geoscience field. Gathering scientists with different backgrounds and expertise has been proven to be the most effective way of solving complex problems. But the most expected outcome of this project is the generation of a new community of geoscientists that are LNLS users. Since the beginning of the project, some activities have been developed to reach its goals. Undergraduate and graduate students from different institutions like Universidade Federal de Viçosa (UFV) and Escola Superior de Agricultura "Luiz de Queiroz" (ESALQ), traditional Brazilian Soil Science schools, have visited LNLS to understand how it works and to have experience in different beamlines, including: Soft X-ray Spectroscopy (SXS), X-ray Powder Diffraction (XPD) and X-ray Absorption Fine Structure (XAFS). One graduate student spent one year with Dr. Hesterberg at North Carolina State University (NCSU) learning good practices to develop experiments with synchrotron radiation. One important achievement of this project is the co-organization of a symposium at the 35th Brazilian Congress of Soil Science, entitled "Application of synchrotron based x-ray absorption spectroscopy techniques to the geoscience field". The symposium includes lectures by Dr. Harry Westfhal Jr. (LNLS) entitled "Introdução às técnicas de análise com luz síncrotron: o presente e o futuro do Laboratório Nacional de Luz Síncrotron", and Dr. Dean Hesterberg (NCSU) entitled "Opportunities for discoveries in Agriculture and Environmental Sciences using siynchrotron X-rays".

Evaluation of zinc distribution in maize seedlings from Zn-treated seeds by synchrotron radiation micro-X-ray fluorescence spectrometry (SR µ-XRF)

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The low concentration of Zn in soils as well as in the diet of some population groups, especially in developing countries, is a common issue. The biofortification refers to increase the concentration of a given element in cereal grains through of fertilizers application in seeds, soil and foliar tissues. In this context, the biofortification of Zn via seeds may contribute to increase Zn levels in plants and, consequently, in food. Although seed treatment is widely used in maize (*Zea mays L.*) for pest and disease control, there is a growing interest to use this technique for plant nutrition purposes. Preliminary studies were performed using synchrotron radiation micro-X-ray fluorescence analysis (SR µ-XRF) in order to elucidate the Zn uptake and its distribution. These studies were used to assess the effectiveness of maize seed treatment with Zn and evaluate the differences in seedlings originated by treated and untreated seeds. Maize seedlings grown by 120 hours were separated in shoots and roots. Roots were separated in three parts: upper, middle and lower. These parts were cut using a stainless steel blade, placed in an acrylic sample-holder and covered with a 4 µm thick Ultralene® film. In addition, cotton pieces soaked with deionized water were used to maintain the plant tissue moisture during analysis. An x-ray microbeam of aprox. 25 µm in diameter was used and the measuring time per pixel was set to 0.4 sec. All experiments were carried out at the D09B XRF Fluorescence beamline of Brazilian Synchrotron Light Laboratory (LNLS) in Campinas, Brazil. Elemental distribution maps were generated using the PyMCA 4.7.4 software. These maps were used to identify the main Zn-accumulation sites in seedlings. Synchrotron radiation µ-X-ray fluorescence spectrometry is a valuable analytical tool for screening purposes, which allows the identification of preferential locations of Zn accumulation in seedlings, aiming for studying its speciation using micro-X-ray Absorption Near-edge Spectroscopy (µ-XANES).

Tender Energy X-Ray Spectroscopy for Determining Phosphorus Speciation in Soils

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Phosphorus (P) is an essential nutrient for all living organisms, but can act as a pollutant when excessive quantities enter aquatic systems. Elevated P levels can cause excessive phytoplankton growth and decreased levels of dissolved oxygen, threatening drinking, recreational, and industrial water supplies. A fundamental understanding of soil phosphorus (P) speciation is vital for understanding P retention and transport in soils. Although the chemistry of P has been extensively studied, specific mechanisms for P adsorption to soils remain largely unclear. Current methods for soil P speciation rely heavily on sequential chemical extractions which are *ex situ* and can introduce artifacts during the analysis procedure. To overcome limitations of current methods for examining the P speciation, non-invasive spectroscopic techniques can be used to analyze soils *in situ*. This study will use tender energy X-ray absorption spectroscopy (XAS) to elucidate bonding mechanisms for inorganic P species at the P K-edge (1.5-4.5 eV). In addition, experiments at the $L_{2,3}$-edge (100-1000 eV) will be used to characterize bonding mechanisms of organic P species. Phosphorus extended X-ray absorption fine structure spectroscopy (EXAFS) data may be used to determine nearest-neighbor identity, bond distances, and coordination number for P. Soils with high (>1000 ppm) P loadings and a variety of chemical and physical properties have been selected from field sites throughout the Chesapeake Bay watershed (USA) to evaluate P speciation. To assess the mobility and bioavailability of P, three soils will be selected for laboratory desorption studies in stirred-flow reactors. Samples from desorption studies will be analyzed with XANES to determine P species present before and after desorption. Initial spectra have been collected at beamline X15B, a tender X-ray (i.e., 1-5 keV) microprobe at the National Synchrotron Light Source, to perform micro-scale XAS and X-ray fluorescence (XRF) imaging at the P K-edge. These studies have indicated the presence of Al- bound and Ca-bound P in soils from the Chesapeake Bay watershed. Additional bulk XANES spectra will be collected at beamlines SXS and TGM at the Brazilian Synchrotron Light Laboratory. Additions to the current knowledge of P speciation from this study will improve understanding of soil P chemistry at a fundamental level and will have implications for P management strategies in eutrophic water bodies around the globe.

The Trigonal Cell Crystallization in Isotactic Poly(Propylene-co-1-Pentene-co-1-Hexene) Terpolymers and Their Competition with Other Polymorphs

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Isotactic polypropylene (as well as its copolymers and terpolymers) shows a very interesting polymorphism. Thus, different entities and crystal contents are observed as function of composition and crystallization conditions. Additionally, a new trigonal form is generated in metallocene isotactic copolymers of propylene with high contents of 1-hexene or 1-pentene as comonomers [1-3].

Moreover, it is possible to combine both comonomers and synthesize terpolymers [4] for studying their different crystalline lattices. Terpolymers based on propylene with 1-pentene and 1-hexene as monomeric units are described in this work, analyzing their interesting polymorphic behavior. This polymorphism and the predominance of the different modifications involved are evaluated as function of composition and crystallization conditions. Real-time variable temperature experiments with synchrotron radiation are a very appropriate tool for studying the nature of the phases involved and the corresponding thermal transitions.

It was found that at high counit contents (approximately more than about 10 mol %), the new trigonal form is also obtained, so that the study of the polymorphism is rather complicated. Specifically, this trigonal modification is in competition with other crystals such as monoclinic and orthorhombic cells for slow cooling rates in the composition interval below 14 mol %. On the contrary, fast cooling rates generate the mesomorphic phase, in competition now with the monoclinic, orthorhombic and trigonal cells, at the same range of compositions.

The disclosure of this kind of competition can be interesting to obtain new properties, develop new products and find new commercial applications.

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X-ray diffraction study of the formation of new structures based on Bi and Se due to heating of the Topological Insulator Bi_2Se_3.

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Bismuth selenide (Bi_2Se_3) is a topological insulator characterized by a crystal network formed by selenium and bismuth atoms. Its structure is lamellar formed by five monolayers of atoms connected by van der Waals interactions, making this material extremely interesting for building new materials like graphene. Its electronics properties are related to other two-dimensional systems, presenting a electronic linear dispersion relationship on selected points of the reciprocal space.

The objective of this work was to observe and interpret the transformations that occur upon heating this material at high temperatures of the order of 620K. To observe these transformations, X-ray diffraction and scanning tunneling microscopy (STM) techniques were used. X-ray diffraction was measured following the 00L and 01L truncation rods. STM observations of the surface of this material were performed while heating inside the ultra-high vacuum chamber with the controller attached to the sample of Bi_2Se_3.

We could observe through scanning tunneling microscopy measurements that Bi_2Se_3 has a perfected hexagonal structure and a five-atomic layer structure with Bi-Se-Bi-Se-Bi monolayers and a terrace height of approximately 1nm. X-ray diffraction measurements reveal that a structural transformation occurs at approximately 570K. New phases are observed one with a similar structure of Bi_2Se_3.

Characterization of Pt_xPd_{x-1}/SiO_2 (x = 1, 0.7 or 0.3) nanoparticles by *in-situ* XAS

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Metal nanoparticles (NPs) have attracted a great deal of attention and have been extensively exploited for their unique optical, electric, magnetic and catalytic properties, which are different from those of bulk materials [1, 2]. In the case of bimetallic nanoparticles, which are particularly important in catalysis, the introduction of a second element allows greater flexibility in the variation of structural parameters by varying the distribution of atoms in the particle. The addition of a second metal facilitates the reduction process, which is typically employed in order to bring the catalyst to the active form [3].

Recent studies of our group have shown that isolated Pt-Pd bimetallic nanoparticles present interesting electronic and structural properties, which implies on distinct catalytic activities during reduction and sulfidation processes [4, 5]. In those experiments, the isolated nanoparticles were submitted to the reduction process in an H_2 atmosphere and subsequent sulfidation in H_2S atmosphere at different temperatures. It was observed that the amount of metal-S bonds in the nanoparticles increases with the quantity of Pd.

In this work, we have studied Pt-Pd bimetallic nanoparticles supported in SiO_2, aiming to investigate the structural/chemical changes of real supported heterogeneous catalysts that were induced by reduction and sulfidation processes. Therefore, we will be able to study the influence of the support in the nanoparticles reactivity. The nanoparticles are produced by chemical synthesis. The Pt_xPd_{x-1}/SiO_2 (x = 1, 0.7 or 0.3) systems were studied by in situ x-ray absorption spectroscopy (XAS) during the reduction by H_2 and posterior sulfidation under H_2S atmosphere, both at 300 °C. The measurements were performed in transmission mode at the Pt L_3-edge at XAFS1 beamline of the LNLS. The evolution of the in-situ XAS spectra of the Pt L_3-edge allowed comparing the bimetallic catalysts with the monometallic one, and it was observed that as higher the Pd amount, higher the samples reactivity with sulfur. The Pt-Pd bimetallic nanoparticles were also characterized by X-Ray Diffraction (XRD) and Rutherford backscattering spectrometry (RBS).

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Electronic Structure of $SrTi_{1-x}Ru_xO_3$

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Metal-insulator transition (MIT) in an intriguing phenomenon in transition metal oxides that can have different driving forces, such as electron correlation, disorder or percolation. The $SrTi_{1-x}Ru_xO_3$ (STRO) series undergoes a MIT for $x_c \sim 0.35$. The end members of the series show completely different physical properties: SrTiO3 (STO) is a diamagnetic band insulator with cubic structure, whereas $SrRuO_3$ (SRO) is an itinerant ferromagnet with an orthorhombic structure. The STRO series has been studied via electrical conductivity and transport measurements [1,2], X-ray photoemission and x-ray absorption spectroscopies [3,4], band structure calculations [5,6] and other techniques. Despite the efforts, the mechanism leading to the transition in this system is still under debate.

Previously, a study on SRO where several spectroscopic measurements were interpreted via an extended cluster model [7] showed that the ground state of this material is dominated by configurations with holes in the ligand band. Now, in order to study the electronic structure of the STRO series, we developed and implemented a double cluster model, in which two octahedra are connected via an oxygen atom. The model includes correlation, covalence and multiplet effects, as well as charge fluctuations between the two octahedra and . The results are compared with X-ray Photoemission Spectroscopy from the literature, and all the spectra were reproduced with a single set of parameters.

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Evaluation of microsampling strategies for the direct analysis of sugar cane leaves by LIBS and EDXRF

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Energy-dispersive X-ray fluorescence spectrometry (EDXRF) and laser-induced breakdown spectroscopy (LIBS) were evaluated for the direct analysis of dried sugar cane leaves aiming at nutrition diagnosis. Phosphorus, K, Ca, S, Fe, Mn and Si were determined by EDXRF by irradiating each leaf fragment in its middle portion with a 5 mm X-ray spot size during 50 s. EDXRF was also used as a tool to infer about the representativeness in the selection of the appropriate number of leaf fragments from the whole diagnostic leaf. It was concluded that 15 leaf fragments (37.5 % of the recommended sampling area) were enough for attaining this purpose. For LIBS, which uses a significant smaller interrogation area for ablation (*i.e.*, 750 µm laser spot size diameter), sampling strategies were selected taking into consideration the distribution of P, Ca, Mg, Fe, Mn, B and Si in 9 mm x 9 mm leaf fragment area. Phosphorus, K, Ca, Mg, Fe, Cu, Mn, Zn, B and Si were determined by LIBS using a rastering sampling approach, where 3 equally spaced sampling lines were analyzed in each leaf fragment impinging 48 accumulated laser pulses per line (Nd:YAG at 1064 nm, 5 ns, 10 Hz, 50 J cm^{-2}) perpendicularly to the leaf midrib. Additionally, it must be stressed that cross-validation between LIBS and EDXRF were performed for P, K, Ca, Fe, Mn and Si presenting high linear correlation coefficients of up to 0.9778 (selecting 15 leaf fragments per diagnostic leaf from 10 different sugar cane varieties). The obtained results reinforces the consolidation of some important concepts of Precision Agriculture and Green Chemistry by providing accurate results towards direct and fast plant nutrition diagnosis.

Imaging the Nucleation and Growth of Nanoparticles in Solution

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A novel microfluidic reactor for *in situ* small angle X-ray scattering (SAXS) and X-ray absorption fine structure spectroscopy (XAFS) of Pd colloidal nanoparticles synthesis is reported. The microreactor allows time resolution ranging from milliseconds to several minutes with a residence time of over an hour. The synthesis of colloidal Pd nanoparticles is investigated in the presence of oleylamine (OLA) and trioctylphosphine (TOP) ligands. For both ligands, SAXS results show the synthesis proceeds through slow, continuous nucleation as evidenced by a continuous increase in the number of particles. Growth is autocatalytic and fast at the early times, then, despite the availability of a large percentage of unreacted Pd precursor, growth slows down dramatically and the Pd nanoparticles diameter reaches a plateau while more nanoparticles continue to form. *In situ* XAFS reveals an increase in Pd-P coordination coinciding with the time of slowed growth. The combined SAXS, XAFS results strongly suggest that the capping ligands play an important role in slowing down growth by binding to the nanoparticle surface leading to a self-limiting nanoparticle size. Despite the slow continuous nucleation and overlapped fast autocatalytic growth, 1nm Pd nanoparticles with narrow size distribution (±20%) can be synthesized using strong capping ligands (e.g. trioctylphosphine).

Synchrotron-based XRD coupled to mass spectrometry to investigate clay minerals dehydroxylation and soil organic carbon oxidation patterns on a gibbsitic Oxisol

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Soils across the globe are reservoir for at least 1600 Pg of organic C within the 0 – 100 cm depth. Plant residues and microbial biomass are the main sources to that C stock, which is accumulated in the form of a complex mixture of organic compounds, collectively referred as to soil organic carbon (SOC). In recent years, SOC has drawn worldwide attention provided its importance in the rise of atmospheric CO_2 levels and associated global warming. Studies suggest that tropical regions may increase its role as a carbon source due to climate change which would be critical as it stores up to 30% of the total global soil C. Therefore, understanding the mechanisms that support SOC stabilization in tropical soils is vital. In soils the combination of several different minerals and organic compounds, together with biological, physical and chemical processes control SOC persistence, which depends mainly on the clay minerals specific surface area (SSA). The most common tropical soils are Oxisols, in which kaolinite is the most common clay mineral, and thus mineral-organic associations may depend more on the content of Al- and Fe- (hydr)oxides, particularly gibbsite, goethite and hematite, which present large SSA. In order to explore the mineral-organic associations and its relationship with clay minerals, we monitored mineral structural changes due to dehydroxylation reactions by applying synchrotron-based XRD and the chemical composition of the volatile byproducts from the organic fraction undergoing heat treatment by means of mass spectrometry. Combined, these techniques helped to assess how thermal decomposition of SOC is related to clay minerals dehydroxylation. The experiment was performed on the XPD beamline at the Brazilian Synchrotron Light Laboratory, in which we probed the samples using X-ray diffraction coupled to the Arara furnace and a mass spectrometer. The samples were a mixture of clay and silt fractions and the associated organic carbon, from a gibbsitic Oxisol from Sao Gotardo – MG, collected at 0 to 10 cm depth without and with the addition of organic C at 4mg g^{-1} soil. These samples were incubated for a year prior to the experiment and for the analysis at the beamline, about 100 mg were used of powdered sample. The diffraction spectra were taken with an energy input of 7 keV between 10 and 50 2θ degrees at room temperature, 105, 300, 600, and 700 °C. Spectra were also taken between 10 and 30 2θ degrees during the ramps between the aforementioned temperatures. The ramps had a temperature increase rate of ~10 °C/min. By accessing the mass spectrometer, we collected m/z ratio data for the following ions: 12, 14, 17, 18, 28, 29 and 44. The mass spectra of the gases evolved from both samples showed high similarity, except on the amount of C released between 250°C and 350°C, where it was observed a higher amount of CO_2 released in the sample with added organic C. At this temperature range, we also observed a steady decrease on the intensity of the gibbsite and goethite peaks, which suggest that fresh added organic C form associations with gibbsite and goethite. The overlapping of the H_2O and CO_2 curves also support the hypothesis of mineral-organic association involving gibbsite and goethite. Release of H_2O and CO_2 is also observed at higher temperatures, probably from kaolinithe, which may indicate that some SOC is associated to this mineral. At higher temperatures, there is no clear difference among the control treatment and the sample in which was applied organic carbon. We conclude that fresh SOC has a higher probability to form interactions with gibbsite and goethite. Since the amount of gibbsite is much higher than goethite in this soil, comparing these minerals is not straightforward and quantitative data for the evolved CO_2 could allow more precise inferences on how each of these minerals affect SOC persistence. Kaolinite may have an important role in SOC persistence despite its low SSA, although the mechanism for this is not yet understood.

Enhanced Dissolution and Transformation of ZnO Nanoparticles: The Role of Inositol Hexakisphosphate

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The toxicity, reactivity and behavior of zinc oxide (ZnO) nanoparticles (NPs) released to the environment are highly dependent on the medium condition. Myo-inositol hexakisphosphate (IHP), an organic phosphate commonly present in the environment, may interact with NPs and generate new transformation products.

In our study, batch experiments were conducted to understand the interaction between ZnO and IHP, or Pi, or IHP and Pi at different pHs and P/Zn molar ratios. The experimental results show that IHP can substantially enhance the dissolution of ZnO NPs. The IHP-induced dissolution and transformation of ZnO NPs (< 0.5 h) is strikingly faster than that in the presence of inorganic phosphate (Pi, > 3.0 h) at pH 7, and the reaction rate increases with decreasing pH and increasing concentration of IHP. Quantitative analysis of the component proportion in the reaction samples is also performed by a linear combination fitting (LCF) of the k space of Zn K edge EXAFS spectra using ZnO and Zn-IHP as reference compounds. The proportion of zinc phytate in the samples increases from 17.6% to 93.6% with increasing IHP-P/Zn molar ratio from 0.1 to 1.0. Zn K-edge XAS spectra of the reaction products formed from the reaction of ZnO NPs with IHP at an IHP-P/Zn molar ratio of 1.0 at different times are also analyzed. Zn K-edge k space EXAFS spectra and LCF results of the kinetic reaction products reveal that the proportion of zinc phytate precipitate increases from 42.7% to 90.6% with increasing reaction time from 1 min to 20 min, respectively. This means that the interaction of ZnO NPs with IHP induces rapid transformation of ZnO NPs into poorly crystalline zinc phytate-like phase (Zn-IHP).

Additionally, our results indicate that ZnO preferentially reacts with IHP when Pi and IHP coexist. This study may contribute to an improved understanding of the role of organic phosphates (e.g., IHP) in the speciation and structural transformation of ZnO NPs as well as in effective remediation of ZnO-polluted water and soils.

In Situ X-ray Absorption Spectroscopy of Molybdenum Sulfide (Mo_xS_y) Catalysts for Hydrogen Evolution Reaction

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Hydrogen Evolution Reaction (HER) is a technological bottleneck in the search for energy carriers capable of storing electricity in the form of chemical bonds. The current catalysts used for this reaction are based on platinum which is too expensive for widespread use. A lot of research efforts are currently focused on developing new catalysts with similar performances than platinum at much lower prices.

Molybdenum sulfides belong to a class of compounds that is active for HER under various stoichiometric formulations. However, the actual structure of the catalysts under functioning conditions is not clear. We have recently shown, using *in situ* X-ray spectroscopy, that a material originally formulated as MoS_3 is converted into a MoS_2-like structure during electrocatalytic HER [1]. In order to better identify the chemical species responsible for HER in Mo_xS_y HER-active compounds, their spectral signatures with various stoichiometries and geometries were screened under catalytic conditions. The S K-edge and Mo $L_{2,3}$-edge spectra of the synthesized compounds were initially measured as powders for reference. Subsequently, each sample was deposited on a screen-printed Mylar electrode by spray casting to characterize its electrochemical and spectroscopic (Mo K-edge, Mo $L_{2,3}$-edges and S K-edge) signatures in an *in situ* electrochemical cell under functional conditions, that is, at acidic pH and under constant reductive potential. Consequently, the local and electronic structures of the Mo centers and S ligands on the film were probed under *pre-catalytic* and *catalytic* conditions in the reduction of protons into H_2 by Mo_xS_y compounds.

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Theoretical Sectroscopy: Excitonic Effects

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Theoretical Spectroscopy group in Ecole Polytechnique, France, is well known for pushing the frontiers of theoretical spectroscopy by developing new foundamental theory of optical properties of materials within the formalism of many-body perturbation theory (MBPT) and time-dependent density functional theory (TDDFT), and creating the codes for high-performance computations.

The group is actively collaborating with synchrotron scientists in the field of photoemission spectroscopy and inelastic X-Ray scattering in both its resonant and non-resonant flavours. Theoretical calculations make possible thorough analysis and deeper understanding of the experimental results, and often make suggestions for new experiments.

One of the recent developements of the Theoretical Spectroscopy group is the methodology for the state of the art treatment of excitonic effects. For many semiconductor applications -- such as photovoltaics and light-emitting diodes -- it is especially important to understand exciton propagation and transport properties that are determined by the energy dispersion as a function of momentum transfer.

As excitons are a truly collective phenomenon, to describe them properly one must use many-body framework and solve the Bethe-Salpether equation that accounts for the interactions between the hole and the electron. The methodology of the ab initio calculations of exciton dispersion in a wide range of momentum transfer for realistic matherials has been developed [1], and the dynamical structure factor and excitonic band structure for a variety of materials have been computed: 2D materials (graphene, graphane), wide-gap insulators, molecular solids, transition metal dichalcogenides and others. The links with experiment are possible thanks to the high momentum-energy resolution of the new generation synchrotron sources.

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Nanocatalysts for the production of H_2 for renewable energy technologies

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The main focus of our research group is the development of nanostructures to be employed as catalysts for the reactions involved in the generation of H_2 from renewable sources, aiming to the application in energy technologies such as fuel cells. Furthermore, our goal is to correlate the properties of the systems with their catalytic activity and selectivity for H_2 production.

The reactions under study so far are chosen to convert sustainable and abundant feedstocks to H_2, such as ethanol, acetic acid and more recently, glycerol, through the steam reforming reaction. To make this H_2 suitable for energy processes, the reformate gas is then purified by the water-gas shift reaction, $(CO + H_2O \rightleftharpoons CO_2 + H_2)$ and subsequently by thepreferential CO oxidation (CO+1/2$O2 \rightleftharpoons CO$2, in the presence of H2 and CO2) [1], both also being part of the reactions under study in our group, as well as the CO oxidation model reaction.

The catalysts being studied comprise a metallic phase supported on a metal oxide. Cobalt and nickel nanoparticles supported on CeO_2 nanostructures with different morphologies are being studied for the ethanol and acetic acid steam reforming reactions, while for the glycerol, vanadium impregnated on Pt/Al_2O_3 systems and Pt-metal alloys are under investigation. As water-gas shift catalysts, copper impregnated on ceria and functionalized ceria nanorods were investigated. For the preferential CO oxidation reaction the catalysts are based on $Pt@CeO_2$ (core-shell nanoparticles), and for the CO oxidation the systems are very diversified and include $Au\text{-}FeO_x$ dumbbels and AuCu alloys supported on SiO_2 and Al_2O_3, and Pt clusters over FeO_x.

Besides the catalytic tests, the characterization of these systems is crucial and several techniques are employed to investigate determinant properties such as the particle size, surface area, reduction degree, adsorption of molecules over the surface, the metal-support interaction and so on. However, for catalytic reactions the possibility to follow *in situ* the eventual changes of the samples under the activation step and reaction conditions can provide valuable information about the behavior of the catalysts under each condition and thus infer about the properties that are having influence on the catalytic activity and selectivity. Therefore, *in situ* experiments have also been a major tool in this group, including synchrotron based techniques such as X-ray diffraction and absorption spectroscopy.

Concerning the research of my PhD project, the focus is the glycerol steam reforming, $C_3H_8O_3 + 3H_2O \leftrightarrow 7H_2 + 3CO_2$, catalyzed by platinum supportedover well-defined metal oxides nanostructures, such as CeO_2, TiO_2, ZrO_2. Glycerol has been receiving much attention for being the main byproduct of the increasing biodiesel production and thus is plentiful and cheap. The glycerol steam reforming and its catalysts however are far from being consolidated in the literature and to make this reaction a route to produce H_2 in large scale, many aspects can be better understood and improved. As examples, to reduce side reaction products (increasing H_2 selectivity), synthetize stable catalysts for the demanded high temperatures (above 400 °C) and avoid catalyst deactivation (due to deposition of carbon species over the surface) [2]. Therefore, the aim of the research is to evaluate the effect of the support and metal-support interface on the aforementioned aspects of the activity and selectivity of the glycerol steam reforming reaction.

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Abnormal Nanocrystallization Behavior in Marginal Glass Forming Alloys

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Marginal glass forming alloys and their nanocrystalline composites are under spotlight for their superior mechanical, magnetic properties and corrosion resistance. Upon devitrification these alloys form an exceptional population of nanocrystals with values up to 10^{24} m^{-3}; a phenomenon that classical experimental and theoretical approaches lack to explain. To unveil the enigma behind this behavior, we present our efforts towards to analyze the as-solidified amorphous and partially crystalline Al-RE (RE=Rare Earth elements) marginal glass forming alloys using state-of the art characterization techniques such as in-situ synchrotron X-ray radiation (HEXRD), transmission electron microscopy (TEM) and atom probe tomography (APT) along with computational techniques such as Reverse Monte Carlo (RMC) simulations. RMC simulations that are constrained with high quality HEXRD data have captured medium-range chemical and topological order in as-quenched amorphous alloys. This observation is further confirmed with APT results. The size and the population of medium-range ordered clusters embedded in amorphous matrix were found to be effective in controlling the nanocrystallization mechanism upon devitrification process.

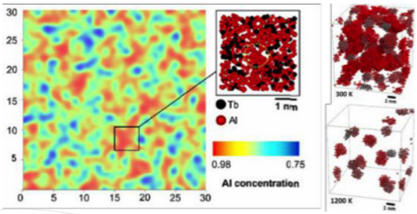

Fig. 1. (a) Atom Probe Tomography (APT) experimental data [1] and the corresponding MD simulations of Al-Tb metallic glass at (b) 300K-solid and (c) 1200K-liquid states.

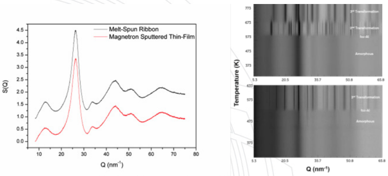

Fig. 2. (a) Total structure factors of melt-spun ribbons and magnetron sputtered thin films of Al-Tb metallic glass. (b) In-situ HEXRD plots of the melt-spun ribbons (top) and magnetron sputtered thin films (bottom) of Al-Tb metallic glasses.

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Switching CoO orientation to manipulate CoO/FePt exchange coupling

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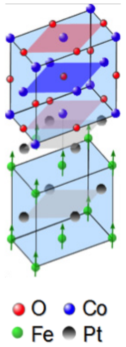
We report here the growth, structure and exchange coupling properties of a ultrathin CoO/FePt double-layer system on Pt(001) with perpendicular magnetization. A previous study on this system reported that reactive Co deposition on Pt(001) and on FePt/Pt(001) gives rise to an epitaxial CoO(111) layer with a slight monoclinic distortion. The CoO(111)/FePt(001) system obtained presents a robust exchange coupling up to the room temperature.[1] By changing the growth process, we succeeded to form an epitaxial CoO(001) layer on FePt/Pt(001). This orientation modification impacts the crystalline structure of the layer, its anisotropies and its coupling with the FePt layer.

Growth and structure have been studied *in situ* and *in real time* by grazing incidence x-ray diffraction (GIXRD) at the BM32 beamline at ESRF, France. The ferromagnetic layer is chemically ordered with the tetragonal *c* axis perpendicular to the surface. The average *c/a* ratio is about 0.93, smaller than the bulk value (0.96). The CoO structure is partially relaxed and presents a tetragonal distortion with a *c/a* ratio around 1.03(1). Its interface with the pseudomorphic FePt layer is rough.

Polar MOKE measurements revealed that the two layers are coupled up to 110-140 K after a perpendicular field cooling. Soft x-ray absorption spectroscopy (XMCD and XMLD) experiments have been performed at 270 K at the ID08 beamline of the ESRF, France. XMCD is sensitive to the ferromagnetic (FM) component of both Fe and Co, while XMLD provides information on the antiferromagnetic (AFM) spin orientation.[2] XMCD shows three contributions to the ferromagnetism of the system: Fe atoms in metallic environment, in oxide environment and metallic Co atoms. During the CoO growth on FePt, a portion of Fe and Co atoms likely exchange their sites. According to XMLD results, Co spins are oriented in-plane. The coupling FM/AFM is then orthogonal



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Synthesis and characterization of Nb_2O_5 and its potential as catalyst for biomass conversion

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The catalytic conversion of cellulose to biofuels and other value added chemicals is one of the most promising routes for the development of economically viable biorefineries. However, the challenge of developing green chemical methods for renewable energy generation based on heterogeneous catalysis relies on a thorough investigation of the physical and chemical properties of the catalyst. In addition, the correlation of these properties to the functional behavior of the catalyst within the cellulose valorization reaction. Cellulose processing firstly requires hydrolysis to obtain glucose followed by the transformed of glucose to fuels and chemicals [1-3]. Thus, this project aims to synthesize a new class of bifunctional catalysts composed of Ni and Co dispersed on Nb_2O_5 for cellulose conversion to obtain platform chemicals such as, sorbitol, HMF and levulinic acid among other products. Solid acid catalysts, such as Nb_2O_5 can be effective for cellulose hydrolysis [4]. On the other hand, transition metals, such as Ni and Co are catalysts for hydrogenation and hydrogenolysis reactions [5, 6]. The structural, electronic, surface and textural properties will be investigated using *ex situ* and *in situ* synchrotron-based techniques (XRD and XAS) as well as N_2 physisorption, XPS and TEM. Acidic properties of the catalysts will be analyzed by TPD – NH_3 and FT-IR using adsorbed pyridine. Physical and chemical characteristics of the catalyst will be correlated with the catalytic performance. This will be a step forward in understanding and optimizing the catalyst and reaction parameters to improve specific product yields.

This project has started 6 months ago and the first step was the niobium oxide synthesis and structural investigation. The synthesis was carried out by the hydrolysis of the niobium chloride to produce niobic acid, followed by a calcination step to obtain the final niobium oxide. The calcination process was characterized by *in situ* X ray diffraction at XPD beamline at LNLS. It was observed that the amorphous niobium oxide starts to crystallize around 500 ^{O}C, first to form a TT phase (pseudo-hexagonal). At about 710 ^{O}C a new phase transition begins and at 750 ^{O}C the T phase (orthorhombic) is clearly observed. Thus, in order to investigate the effect of calcination temperature in the surface and textural features were selected the calcination temperatures of 400 ^{O}C (amorphous – Nb-400), 550 ^{O}C (TT phase – Nb-550) and 750 ^{O}C (T phase – Nb-750). It was noticed that the surface area decreases as the calcination temperature increases.

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Incremental Reconstruction Methods and Log-Polar Coordinates Applied intomographic reconstruction

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The problem of tomographic image reconstruction involves a large amount of data, thus fast and efficient methods are much important. Currently, commercial CT scanners use the filtered back projection method (FBP) [2] due to quality in the obtained images. However, the computational cost to reconstruct a image of dimension n^2 is $O(n^3)$, which is concentrated in the backprojection, while thefiltering operation cost is $O(n^2 \log n)$, and it is calculated using FFT's [4].
Another approach to the tomographic image reconstruction is to assume that the function to be reconstructed is a finite dimension space and to solve a linear system using iterative methods. The algebraic reconstruction technique (ART) is one of the most classic methods [5]. The conditioning of the system matrix combined with the errors contained in the scanner data affect directly the quality ofthe reconstructed image. Thus, more advanced strategies have been developed to reduce these errors, as the statistical model for positron emission [8]. Overall, the noise in the case of iterative methods is lower compared to FBP, but its influence increases with the number of iterations. Moreover, faster algorithms are required in order to reconstruct images in a few iterations, considering that eachiteration cost is $O(n^3)$.
In order to speed up the iterative methods, the incremental algorithms were developed such as OS-EM [6], BRAMLA [7] and BSREM [3], among others. In this context the method which is an application of the interpolation of the Radon transform in a log-polar grid is presented, where FFT algorithms can be used in order to compute efficiently projections/back-projections of parts of the data. Considering log-polar coordinates [1], we can write the Radon transform as a convolution. Performing these convolutions in Fourier space, by algorithms FFT, we can get a quick method for calculating the projection, and transposing and reversing the order of steps, the back-projection can be calculated efficiently. This method has a time complexity of $O(n^2 \log n)$, the same as other fast reconstruction algorithms.

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Observing magnetic cobalt clusters underneath graphene on SiC(0001) in real and reciprocal space.

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The behavior of Co nanoparticles (NPs) grown on graphene/SiC(0001) after oxygen exposure and heating in ultrahigh vacuum was investigated [1]. The results of Photoelectron Spectroscopy (XPS) show that, as grown, the metal is on the surface of the graphene/SiC and suffers oxidation forming a single phase CoO when exposed to O_2, even at low doses ($\sim 10^{-7}$ mbar). After heating in ultrahigh vacuum (UHV), there is a deoxidation of cobalt and intercalation between the graphene (G) and the buffer layer (BL), as indicated by XPS. Scanning Tunneling Microscopy (STM) images show that cobalt forms almost regular small 2D clusters between G and BL. Moreover, graphene acts as a barrier to oxidation, preserving the metallic and the magnetic character of the material even when reexposed to O_2 ($\sim 10^{-5}$ mbar). We applied a synchrotron-based Photoelectron Diffraction (XPD) [2,3] technique to elucidate the relative positions between cobalt and carbon atoms. The preliminary results will be presented. The possibility to produce large-scale graphene-capped ferromagnetic clusters (or films) assembled on a semiconductor substrate has enormous potential for technological applications, for example, in magnetic data storage media or other devices.

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Stabilization of ZnO(0001) Ultra-Thin Films on Metals: Reconstruction vs Hydroxylation

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Ultrathin (0001)-oriented films of ZnO on noble metals have recently been found to exhibit interlayer relaxations resulting in the hexagonal BN-like crystal structure[1]. Apparently, the driving force for such reconstruction is polar instability of either (Zn- or O-terminated) surfaces. Here[2]_ENREF_2_ENREF_2, we examined surface hydroxylation as another possible stabilization mechanism. The zinc oxide films grown on Pt(111) and Ag(111) supports were studied by infrared reflection absorption spectroscopy as a function of the film thickness and morphology imaged by scanning tunneling microscopy. Although prepared in oxygen ambient, the "as grown" films on Pt(111) all revealed hydroxyl species. In contrast, the bilayer films on Ag(111) did not expose OH, not even upon dosing of hydrogen or water. The results show that hydrogen may efficiently be provided by a Pt support, even for the relatively thick films, via hydrogen dissociation and subsequent diffusion of H atoms through the film. Thermal stability of the OH-terminated surfaces was found to depend on the film thickness, with a monolayer film being the least stable. Removal of OH species from a monolayer film proceeds through water desorption, and may be accompanied by hydrogen spillover onto more stable multilayer islands. It appears that stabilization of polar ZnO surfaces in the form of metal supported films is a delicate balance between interlayer relaxation and hydroxylation.

The submonolayer Zinc Oxide islands grown on Pt(111) transfers into a so called 4x4 honeycomb structure upon dosing trace amount of H_2 at room temperature[3]. CO poisoned surface does not reveal the same phenomenon. Neither is the phenomenon observed on the submonolayer Zinc Oxide islands grown on Ag(111). These observations suggested that the H atom, which comes from the H_2 molecules dissociates on the Pt(111), induces the transformation. In the STM movie, high extend of mass transfer revealed during the transformation suggests that some kind of mobile species is involved in the transformation.

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Synthesis and Characterization of Magnetic Nanoparticles growing on Porous Alumina Template

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Magnetic nanostructures are currently of high scientific and technological interest in a variety of different fields. Some of the applications include ferrofluids, spintronics, directed assembly, as well as for imaging and therapeutic applications. The interest in these nanostructures is due to the unique physical properties not seen in the bulk materials. Many different methods have been reported for obtaining magnetic nanostructures. Among them, template-assisted methods for fabrication of magnetic nanomaterials, have received a special interest due to the capability of obtain 1D nanostructures (nanowires and nanotubes). These methods, involves the use of a nanoporous material (e. g. alumina) which is filled in by a physical or chemical process. Electrodeposition and infiltration are methods primarily employed to fill the cylindrical nanopores with magnetic materials. Less attention has received the fabrication of magnetic nanoparticles embedded in porous templates, mainly due to the formation of continuous structures inside of the pores. However, Kanamadi et. al [1] have suggested that infiltration methods in small pores produce discontinuous magnetic nanowires. Non-uniform nanopore size (along the pore axis), and the drying and decomposition of the precursor solution are accepted to be the main causes. The result is a 1D magnetic nanostructure with a wide distribution of lengths and in some cases the formation of insulated nanoparticle. This study described a simple method for fabrication in situ of magnetic nanoparticles embedded into a porous Anodic Aluminum Oxide template (AAO). For this, an aqueous solution of iron and cobalt salts was infiltrated in an AAO template. During the process a vacuum was used to allow the pores to be filled. The precursor solution inside of the pores was treated thermally for the magnetic phase formation. The structure of the as-prepared samples was studied by x-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The composition of the samples was analyzed by energy-dispersive x-ray spectroscopy (EDX). The magnetic properties were measured by SQUID in ZFC-FC mode at room temperature and at 5 K for hysteresis loops. The results confirm the presence of magnetic nanoparticles (cobalt ferrite), with a crystallite size between 10 and 20 nm. Nanoparticles were embedded inside of AAO template with ellipsoidal shape (prolate). The ellipsoidal diameters along the long and short axis are in agreement with the crystallite size and the pore diameter of the template. Magnetocrystalline anisotropy is at least one order of magnitude larger than the shape anisotropy. That is why the hysteresis loops are the same when the sample is measured with applied field in parallel and perpendicular geometry at pore axis. ZFC-FC measurements reveal that the system is superparamagnetic, with a wide distribution of nanoparticles sizes and an average blocking temperature of 436 K.

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Hot hardness testing: the use of coupled aging heat treatment and Vickers hardness to predict phase transformations in Ti-Nb-Fe alloys

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Titanium β metastable alloys are widely used among other things due its possibility to improve the mechanical properties by aging heat treatments [1]. In the last years numerous researches aimed optimize new Ti alloys by effects of aging heat treatments on the microstructure and consequently on the mechanical and physical properties have been reported [2-3]. The aim of this work was to use hot hardness test coupled with isothermal aging heat treatments to predict phase transformations in Ti-Nb-Fe alloys. The Ti-30Nb-xFe (x= 0, 1, 3, 5 wt.%) alloys investigated in this study were prepared by standard arc voltaic melting, homogenization, hot rolling, solution heat-treatment followed by water-quenched procedures [4]. Predictions of phase transformations and mechanical behavior were evaluated by hot temperature Vickers indentations using a homemade furnace operated with a load cell of 500 kgf and a diamond indenter. Transmission electron microscopy (TEM) images were obtained from FEI/Philips CM-200T (200 kV LaB6) using thin foils prepared in the FEI Helios NanoLab™ 600 DualBeam (FIB/SEM). The hot hardness results showed all alloys behaved similarly to each other without significant gain hardness in the early stages of aging. However, for higher time aging Ti-30Nb, Ti-30Nb-1Fe and Ti-30Nb-3Fe alloys showed hardness values above 300 HV. The Ti-30Nb-5Fe alloy was the exception and showed virtually no increase in hardness for the aging studied times. TEM/SAD results showed that increase of hardness is mainly due the omega phase nucleation and growth. Otherwise no omega growth was observed in Ti-30Nb-5Fe. The results allow to conclude that the hot Vickers hardness test coupled with aging heat treatment are a powerful tool to predict phase transformations and consequently to design experimental aging routes.

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Unveiling ancient life with the use of synchrotron light and spectroscopic techniques

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The application of novel analytical techniques to the study of ancient life is enabling new and more sophisticated scientific problems to be attacked in paleobiology, allowing the access of chemical and morphological information, and helping to distinguish biogenic from taphonomic (*post mortem*) alteration data. These advanced analytical techniques, mostly nondestructive, applied to paleobiology studies originated a new field of research, the paleometry[1]. Here we present a series of synchrotron light and spectroscopic techniques that are being successfully employed at the Brazilian Synchrotron Light Laboratory (LNLS) to characterize fossil samples and help to scrutinize evolutive and anatomic questions of paleontological data, besides early life identification studies. Through spectroscopic techniques as X-ray Fluorescence (XRF), X-ray Absorption Near Edge Structure (XANES) and Energy Dispersive X-ray spectroscopy (EDX) we could successfully identify matrix and fossils components, observing anatomical distributions of elements associated with biogenic origin, and obtaining information about the chemical composition of the environment during the fossilization process. Complementary, imaging techniques as micro-CT and Scanning Electron Microscopy (SEM) provided high-resolution morphological information of internal preserved structures without sample damage, allowing studies with anatomical precision, and even the evaluation of soft tissues preservation. Raman and Infrared (IR) spectroscopies were able to identify chemical bounds, providing information about the state of preservation of biomolecules and of fossil and matrix chemical composition.

Together, these approaches can largely contribute for understanding ancient life, although refining taxonomic data and cladistics, and can also help recreating more accurately paleoecological and paleoenvironmental scenarios, as well as allowing studies in experimental taphonomy, down to the molecular scale.

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EUV and X-ray Holography with tabletop sources and free electron lasers

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We describe experiments that utilize the coherent flux from a tabletop and a free-electron laser (FEL) to perform coherent x-ray imaging with Fourier transform holography. Two experimental geometries are investigated capable of femtosecond temporal and nanometer spatial resolution . For the tabletop laser, a Fresnel zone plate is placed up-stream from the sample[1] (Fig.1). The Fresnel zone plate increased the reference photon flux and enabled single-shot imaging. For stability, the FEL experiment utilized a reference hole that is fabricated directly into the sample mask. The interference of the reference and object beams provided a simple and fast reconstruction procedure of the real-space image. The data is obtained using an FEL (FERMI) and an extreme ultraviolet tabletop laser that have high degree of coherence making them well suited for coherent imaging. The FEL experiment investigated ultrafast demagnetization effects of magnetic domains in a pump-probe configuration. The imaging utilized X-ray circular dichroism at the M-edge of Cobalt to reconstruct the magnetic contribution of the sample [2].

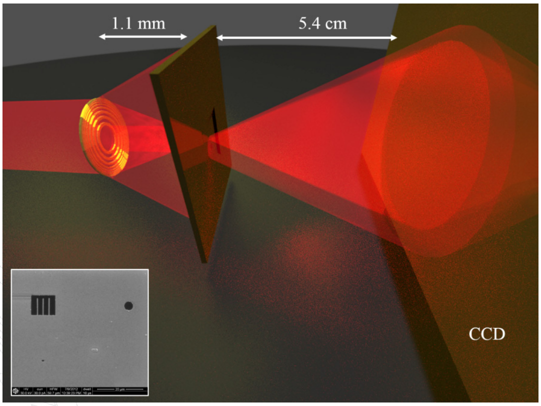

Figure 1: A diagram of the experimental geometry that utilized a Fresnel zone plate to increase the reference wave photon flux for Fourier transform holography.

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Mg-doped ZnO QDs incorporated in lipid-based systems for bioimaging

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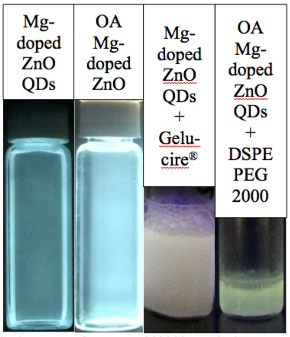
ZnO quantum dots (QDs) have gained attention as potential labels for bioimaging and theranostic applications because of their tunable luminescent properties, biodegradability and very low toxicity in vivo [1]. In the present study, ZnO QDs doped with Mg^{2+} ions, reported to enhance the luminescence of ZnO, have been synthesized using the sol-gel route and their surface capped with oleic acid, to provide them colloidal stability in non-polar environments and to promote their later incorporation into lipidic systems. Indeed, lipid-based systems are currently exploited as nanocarriers of many drugs, improving their bioavailability and reducing side effects [2].

As evidenced by time-resolved synchrotron SAXS measurements, the dopant ions strongly influenced the growth and final size of ZnO nanocrystals but the ZnO wurtzite lattice was preserved up to a 20 mol% nominal concentration of Mg^{2+} ions in the reaction medium. With proportions of Mg^{2+} ions increasing from 2.5 to 20 mol%, both the absorption and emission spectra of the QDs experienced a blue shift. The 20% Mg-doped ZnO QDs presented the better quantum yield (~ 60%), about 6 times higher than that of the ZnO suspension (~10%) [3]. These QDs have been loaded into Gelucire® nanoparticles or DSPE-PEG micelles, showing visible fluorescence, promising for *in vitro* imaging.



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X-Ray Raman Scattering from the lithium K-edge in LiH

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A study of the excitation spectrum of core electrons of Li in LiH for low momentum transfer, using high resolution inelastic x-ray scattering, is presented. Measurements were carried out at the XDS beamline of LNLS. The core electron contribution was extracted from the whole excitation spectrum and the analysis is accomplished by means of ab initio simulations using FEFF code [1]. The near edge fine structure of the spectrum is interpreted in terms of excitation channels allowed for dipole transitions and the symmetry-projected density of empty states. Core-hole effects were found to be appreciable and need to be taken into account in the simulations in order to reproduce the measured spectral features. A Li K-edge chemical shift of 2.2eV to higher energies relative to Li metal was observed [2].

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Quantification of the critical dose for radiation damage to perfluorosulfonic acid using soft X-ray microscopy

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The rate limiting reaction in polymer electrolyte membrane fuel cells (PEM-FC) occurs in the cathode catalyst layer at the triple-phase boundary between the catalyst and electron conductor (Pt or Pt-alloy on carbon nanoparticles), the proton conductor (perfluorosulfonic acid (PFSA) ionomer) and the gas (transport of O2 and H2O through the porous structure of the carbon nanoparticles). The ionomer distribution affects the performance of PEM-FC and its optimization can decrease use of the expensive Pt/Pt-alloy catalyst nanoparticles. Analytical microscopies such as TEM-EELS, TEM-EDX and Scanning Transmission X-Ray Microscopy (STXM) provide a means to analyse ionomer distributions [1]. However, radiation damage by ionizing radiation (electron beams or X-rays) limits visualization of the distribution of ionomer at the nanoscale. In order to develop measurement protocols which minimize errors due to damage it is helpful to know the critical dose for radiation damage, which, along with careful evaluation of doses associated with different methods, can lead to more reliable analytical imaging of ionomer in PEM-FC cathodes.

For this work the critical dose is defined as the dose for which the intensity of a characteristic spectral feature of PFSA is reduced by 1/e (or a spectrl feature of a damage product is increased by 1/e reltive to a saturation level). Here, we quantifed the critical dose for damage by ionizing radiation using a focused (~32 nm) soft X-ray beam of STXM in the Advanced Light Source. 9-pad patterns were exposed in uniform regions of the membrane of an activated CCM sample using different exposure times and X-ray energies. Post patterning images at 292.4 eV (C1s ® σ^*_{C-F}) or 692.6 eV (F1s ® σ^*_{C-F}), as well as full C 1s and F 1s image sequences were used to quantify the spectral changes in each pad and thus the relative damage. Four different analytical methods were used to determine the critical dose. The results were similar within non-systematic uncertainties, yielding an averaged critical dose of 5±3 MGy. This is by far the lowest critical dose reported for polymeric materials to date. The next most sensitive material is polymethylmethacrylate (PMMA) which has a measured critical dose of 67±10 MGy [2]. This quantitative measurement, the first for PFSA to our knowledge, emphasizes the challenges of making analytically meaningful measurements of ionomer spatial distributions, especially at the highest spatial resolution scale, where the dose used increases substantially.

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Determining the true colors of the first Gondwana bird: Synchrotron x-ray micro tomography analysis of Araripe Basin fossils

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X-ray synchrotron imaging techniques are the new frontier for the paleontologist, because they enable the study of fossils with a new methodology approach, which allows a non- destructive detailed view of internal or even histological fossil structures. As a non-destructive method it is well suited to the study of highly valuable single specimens, as are the case of many samples of Brazilian fossils. In South America, the Aves occurrence is represented by many taxa, including basal birds like Enantiornithes and derived taxa including Neornithes. However, in Brazil, there are only three Cretaceous birds, recognized by fragmentary bones from the Bauru Basin, but none yet described as formal species. In the Santana Formation (Crato Member, Aptian-Albian) the fossil Aves occurrence is still debatable, because fossil remains are generally represented by isolated feathers, which can either belong to birds, or to theropod dinosaurs [1]. However, this situation has recently changed because we now found a complete specimen from this lithostratigraphic unit. The objective of this study is thus to analyze in the best possible fashion the paleobiological aspects of this first Araripe Basin bird, including the potential description of its ornamental patterns in feathers. This would to infer the origins and possible bird morphotypes from the Lower Cretaceous of Gondwana. The complete specimen is deposited in the Paleovertebrate collection of the Geology Department of the UFRJ under de collection number UFRJ-DG 31-Av from the Araripe Basin (Santana Formation, Crato Member). The specimen consists in an almost complete skeleton partially articulated with impressions of feathers preserved in mold and counter mold. It also includes the skull, fore and after limbs, scapular and pelvic girdle and vertebrae. Our investigation will also include isolated feathers (n = 18) found in carbonate samples from the same lithostratigraphic unit. We intend to apply synchrotron x-ray techniques to characterize possible chemical residues of melanin pigments, which could allow inferences about colors and color patterns [2, 3].

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Poorly crystalline nanoparticles formed in arsenic-bearing mine tailings in Zimapán, Mexico

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Heavy metals unearthed during mining operations can be found in mine tailings and raise concerns for making remediation difficult and expensive. This is an ubiquitous problem in palces with tailings that are rich with sulfide minerals that will easily oxidize and create acid mine drainage (AMD). Arsenic, zinc, lead, copper, nickel and many other heavy metals are major concerns of acid mine drainage. The heavy metalloid arsenic is ubiquitous to natural soils and occurs in multiple oxidation states, generally As(III) and As(V), capable of forming organic oxyanions and the atypical inorganic form. Arsenic-bearing colloids and nanoparticles , various iron oxides, and silica present are susceptible to the dynamic environmental changes because of their large surface area, structural defects, and incorporation of several elements into their structure. To alleviate low acidy and reduce contaminant mobility, liming is a common and cheap option. The study site in Zimapán, Mexico is abundant with limestone and should in theory not have a AMD problem. Unfortunately, our knowledge on these reactive particles in the limestone environment or the liming reclamation areas is very limited due to the difficulties of characterization of these materials with common methods and instruments.

The general objectives of this study are: 1) to characterize these nanoparticles and colloids on the atomic scale and their transformations in a limestone environment, 2) to characterize As speciation in each associated solid phase and the mobilization and transformation of As associated with the mineral phase conversions, and 3) to model the reactivity of the nanoparticles and the As geochemistry in the limestone environment.

The region in Hidalgo state, Mexico has seen mining since the late 1500's and has historically been mined for Pb, Zn, and Ag. The mine tailings Zimapan, Mexico offer an excellent model to systematically investigate the geochemical processes of the heavy metals. Lack of regulations have lead to these kind of areas and now require remediation to avoid damaging environment impacts. Understanding the mine tailing composition is one of the initial steps of such an endeavor. Tailing and soil samples have been collected, fractionated, and characterized with a series of spectroscopic methods including X- ray diffraction, micro-beam extended X-ray absorption fine structure spectroscopy, X-ray absorption near edge structure, and high-resolution transmission electron microscope.

The samples exhibited a pH near 2, and indicated high mineral heterogeneity among one another. X-ray diffraction, along with other methods, confirmed samples to contain an abundance of iron oxides such as ferrihydrite, goethite, lepidocrocite, and plumbojarosite in the oxidized tailings. In addition, pyrite, gypsum, orthoclase, muscovite and quartz were also present as residues. One sample of almost pure scorodite contained over 100,000 ppm of As. X-ray absorption near edge spectroscopy data was collected at the National Synchrotron Radiation Research Center, Hsinchu, Taiwan and also at Argonne National Laboratories, Chicago, Illinois, USA. The XANES experiments unanimously indicated that arsenic occurred as arsenopyrite form in the original tailing, but was oxidized to form arsenate in an intimate association with nanometer-sized iron oxides. It was determined that the majority of the As in the samples persist as As(V). There is also evidence of samples having both forms of Arsenic (As(III) and As(V)) together.

Sedimentological, geomicrobiological and geochemical study of modern and fossil travertines in the Los Hornos hot spring, Southern Puna of Catamarca, Argentina

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The term “travertine” and “tufa” usually refers to non-marine carbonate precipitates formed in or near springs, rivers, lakes and caves, with a diverse range of fabrics and textures, from crystalline to micritic and grumulous. Its mineral composition, mainly calcite and/or aragonite, constitute a record of the water chemistry, hydrology and climate, physico-chemical and biological processes. The presence of microorganisms in these systems requires the understanding of the interactions between microbes and minerals, their influence on nucleation and crystal growth and chemical signals preserved in them, particularly processes relevant to microbial scale (micro and nano scale).

Travertine and tufa are recognized for their properties as ornamental and application rocks, as sources of chemicals for industrial applications and as paleoclimatic records, so their mineralogical and geochemical characterization is of great importance. The recent discovery of microbialites and travertine systems with unusual petrophysical properties (extreme porosity and permeability) and as hydrocarbon deposits in the *Pre-Salt* of the *offshore* basins of Brazil highlights the need to have a deep understanding at different scales of the processes that control their formation, distribution and physical-chemical properties.

Due to the above, our project focuses on the study of active and fossil hydrothermal travertine systems located in the Los Hornos hot spring, Southern Puna of Catamarca, Argentina. The travertine of Los Hornos hot spring, are located at the eastern end of the San Buenaventura range (26° 52’ 59.84”S, 67 ° 45’ 59.52” W; 3500 m). The basement of southern Puna is represented by metasedimentary rocks and ortogneisses intruded by Lower Paleozoic granites. Above the basement in non-concordance lie continental red series (Upper Eocene-Miocene) interpreted as the development of the foreland basin. Upper Miocene and Pleistocene ignimbritic series lie unconformably on the rest. In this context develop hydrothermal events that give rise to the hot springs and Los Hornos travertine, where upwelling systems or vents, ponds with microterracetas development, pisolitic acumulations and staggered fluvial travertines are distinguished. The vents are colonized by groups of extremophile microorganisms (photo- and chemo-trofos) controlled by changes in pH (average 6.5) and temperature (up to 65 degrees); with precipitated carbonate minerals, salts and oxides of Fe.

The main objective of our project is to conduct a detailed and high-resolution sedimentological, geomicrobiological, petrographic-petrophysical and geochemical study of active travertine and tufa systems to understand processes of formation, and to make comparisons and analogies with similar examples of the geological record. This is intended to make comparative analyzes and build a model of development of the different textures and structures and geochemical signals there, preserved with special emphasis on the understanding of the microbiological and physico-chemical processes under study. Using high resolution techniques that allow textural and geochemical studies (SEM, TEM, SIMS, and spectroscopic techniques using light Syncthoron) is central to our approach because they allow a better understanding of the interactions between microbes and minerals to a deeper understanding of the controls in textural and chemical preserved signals.

Abstract for the SyncLight 2015

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Ferroelectric materials have attracted the attention of the scientific community not only for the fundamental questions still open about their behavior, but also due to their great potential for use in electronic or spintronic devices.

In this contribution we present results obtained so far during our PhD work at the Brazilian Synchrotron Light Laboratory (Laboratorio Nacional de Luz Sincrotron) concerning the dynamics of BaTiO3 ferroelectric domain walls. We will present the observation of ferroelectric domains by Piezoresponse Force Microscopy (PFM) and by Photoelectron Emission Microscopy (PEEM) using ultra violet radiation.

Peeking at the Mechanisms of Sensor Response and Environment-Induced Degradation of Device Performance

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Gas adsorption on solids plays a critical role in the operation of solid state gas sensors and is a primary driver for the degradation of electronic devices. Developing accurate adsorption models is difficult because of the large number of variables that influence gas adsorption kinetics, including adsorbate and adsorbent species, adsorbent surface area, gas pressure, temperature, and incident light intensity. In an effort to characterize the influence of each of these variables on adsorption kinetics and measure the effect of adsorption on electronic device performance, we have developed an environmental system which allows for in situ electrical device characterization while pressure, gas species, gas flow rate, temperature, and light intensity can be systematically changed. A quartz crystal microbalance inside the chamber makes it possible to measure both adsorption isotherms and the dependence of device performance on adsorbed mass for different adsorbates and adsorbents. Here, we present results from some initial studies on the influence of humidity on the electrical properties of both zinc oxide films and carbon nanotube films. Future development of the system will include optical (Raman, photo- and electro-luminescence, and absorbance) techniques to realize full electro-optical characterization for in situ diagnostics. Once optimized, the system will be replicated at the neutron beam line to enable full structure-functional characterization of thin films for broad range of applications.

This research was conducted at the Center for Nanophase Materials Sciences and the Spallation Neutron Source, which are DOE Office of Science User Facilities. Synthesis, purification, and preliminary characterization of materials were supported by the Laboratory Directed Research and Development program. Financial support comes from the Bredesen Center at University of Tennessee.

Investigation of Chiral Asymmetries through Photoelectron Circular Dichroism: the case of Camphor and Fenchone

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Chirality, the characteristic non-superimposablility of some objects onto their mirror image, has long been of interest. It is omnipresent in nature: from the macroscopic human hands, to microscopic phytoplanktons to the molecular level in drugs, amino acids, pheromones, DNA, etc. Pasteur's hypothesis of the existence of homochirality in nature led to a physical investigation of molecular chirality. A popular technique for such measurements is circular dichroism (CD). However, CD has the limitation of being used mainly for non-dilute samples in the liquid phase, and is also very weak in intensity, creating a need for other chiroptical probes.

Photoelectron Circular Dichroism (PECD) is an intense forward-backward asymmetry observed in the photoelectron angular distribution (PAD) with respect to the axis of propagation of light when randomly oriented gas phase pure enantiomers are ionized by Circularly Polarized Light (CPL).

PECD was predicted 40 years ago however, it was only in 2000 [1] that realistic theoretical computations showed that PECD, which is electric dipole allowed, is both orbital-specific and continuum state dependent showing large values of asymmetry (order of magnitude more intense than classical CD). This asymmetry happens to be very sensitive to the whole molecular potential including conformers, clustering and vibrational dynamics [2].

The tunability and stability provided by synchrotron radiation (SR) facilitates a comprehensive study of the dynamic richness of PECD. The high flux, polarization control and purity of the SR provided by the VUV beamline DESIRS[3] associated with a double imaging electron-ion coincidence spectrometer (i^2PEPICO) [4] makes this facility unique for PECD studies.

We used such a facility to study the PECD of the terpenes fenchone and camphor, geometrical isomers which differ in the site of attachment of two methyl groups. While their photoelectron spectra are very similar, they show strongly different PECD and even a quasi-complete reversal of their respective chiral asymmetries in the threshold region, making PECD a structurally sensitive probe for chemical substitution which might be used in an analytical context.

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Crystallographic and electronic characterization of $(La,Sr)(Ti,Co)O_3$ oxides for symmetrical solid oxide fuel cell electrodes by synchrotron X-ray diffraction and hard X-ray absorption spectroscopy

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The Symmetrical Fuel Cells (SSOFC's) concept has been reported as a particular SOFC configuration where the same compound is used as anode and cathode. This design has inherent benefits over traditional SOFC since it could solve two of their main problems, sulfur poisoning and carbon deposits (when hydrocarbons are used as fuel), by simply inverting the gas flux and, improving the long term stability. Another benefit is the design and manufacturing simplicity. In the other hand, requisites on SSOFC electrode compounds are more restrictive than in normal cathode or anode materials since it has to fulfill both requirements simultaneously.

Although $(La,Sr)TiO_3$ oxides (LST) have been reported as a possible SOFC anode materials, and $(La,Sr)CoO_3$ is considered as a SOFC cathode with excellent properties, the possible solid solution LST-LSC remained mostly unexplored. In this work, this solid solution is studied in the search of a possible SSFOC electrode. In particular, a complete characterization on $La_{0.4}Sr_{0.6}Ti_{1-y}Co_yO_{3\pm\delta}$ (LSTC) oxides is presented.

LSTC structural properties were obtained from synchrotron X-ray powder diffraction (XPD) at room temperature. A slight distortion from ideal cubic perovskite Pm-3m due to the rigid rotation of oxygen octahedral around transition metals (TM) was observed on all samples, being related to the freezing of an only one symmetry mode ($R5^-$) and leading to the rhombohedral R-3c space group. Structural properties at electrode working environment were also evaluated, a reversible R-3c to Pm-3m second order phase transition was found on all samples, both in synthetic air and diluted H_2 atmospheres. A direct correlation between transition temperature and structural distortion was noted. Also, the compound charge compensation through perovskite A-site vacancies was found to be the main process for charge compensation for low cobalt content ($y < 0.3$). This was followed by the Sr occupancy factor ranging from [Sr] = 0.4 for y = 0.0, expected for a low temperature synthesized LST, to the stoichiometric [Sr] = 0.6 for y = 0.3. Complementary, Neutron Powder Diffraction has been also performed on selected samples to confirm oxygen atom positions and thermal parameters.

The local environment around the perovskite B-site was studied by Extended X-ray Absorption Fine Structure spectroscopy (EXAFS) in order to compare it with the atomic ordering observed at longer scales by X-ray and neutron diffraction. This analysis confirmed the model of the oxygen octahedra rigid rotation around the TM. Additionally, Ti-O distance was found to maintain a stable value as Co content was increased, but a difference between Ti-O and Co-O distances was noted for low cobalt content being greatest (~0.1Å) for y = 0.1 and decreasing down to be almost zero for y = 0.5.

Electronic structure was also evaluated through the analysis of X-ray Absorption Near Edge Spectroscopy (XANES) on Ti and Co K-edge data, combined with EXAFS results and Density Functional Theory (DFT) calculations. Oxidation states of TM could be inferred from their absorption edge energy followed by a calibration with well-known compounds having the same symmetry. In this way, Ti oxidation state was found to be +4, remaining stable in all the compositional range. On the other hand, Co XANES spectra have a strong influence from Co-O distance variation for $y \leq 0.5$ which affects the crystal field and, therefore, the atomic orbitals splitting. DFT calculations, coupled with XPD and EXAFS results, successfully modeled the samples XANES spectra, even though they show a remarkable energy shift. In this sense, a more qualitative approach leads to identify Co valence state as +3 in that compositional range.

The correlation between all these complementary measurements and analysis is also discussed, aiming to understand the origin of the LSTC electrochemical properties as a SSOFC electrode.

Development of $SiO_2@TiO_2$ core-shell nanocomposites for application in photocatalysis

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Growing attention is dedicated to research of photocatalytic processes promoted by TiO_2 as they offer an interesting, sustainable and promising approach for environmental remediation and solar energy conversion processes [1]. TiO_2 photocatalytic activity closely depends on physical properties such as surface area, crystallinity, morphology, particle size and crystalline phase of titania, with anatase being the most active photocatalytic polymorph of TiO_2. In order to make possible the use of TiO_2 photocatalyts in different applications it is important to develop synthetic strategies that allow control over such physical properties, especially in the case of nanometric TiO_2, which suffers from drawbacks such as tendency to agglomeration, phase transformation and decrease in surface area upon thermal treatment. Furthermore, stabilization of TiO_2 in anatase form at high temperatures (T > 800°C) avoiding anatase-to-rutile transformation is required in applications that involves high temperature processing (e.g. self-cleaning coatings and photocatalytic ceramics). Aiming to address these issues, our group is currently researching synthetic strategies for the deposition of TiO_2 nanocrystals over silica particles, leading to the preparation of $SiO_2@TiO_2$ core-shell nanocomposites [2]. Such nanocomposites can be prepared by the grafting and controlled hydrolysis of titanium alkoxides on the surface of silica particles dispersed in ethanol/isopropanol mixtures. Crystallization of the deposited amorphous titania into anatase nanocrystals is achieved by a soft hydrothermal treatment. Electronic microscopy analysis evidences uniform coating of SiO_2 spheres (mean size 200 nm) with a TiO_2 shell constituted of 5 nm titania nanocrystals. Compared to unsupported TiO_2 nanoparticles of similar size, the $SiO_2@TiO_2$ nanoparticles exhibit superior photocatalytic activity, which is attributed to the better dispersion of the silica-supported anatase nanoparticles, improved adsorption of organic molecules near the photoactive sites and increase light harvesting efficiency due to the core-shell morphology. Additionally, the anatase TiO_2 supported on silica particles presents remarkable thermal stability, remaining stable and not being converted into rutile even after calcination for 2 hours at 1200°C. Thus, the $SiO_2@TiO_2$ nanocomposites present great potential for technological applications, being especially interesting for the development of thermally stable anatase TiO_2 self-cleaning coatings and photocatalytic ceramic tiles for environmental applications. Finally, we are currently working on strategies to introduce vanadium and nitrogen dopants into the TiO_2 nanocrystals lattice in order to allow visible light absorption and further improvement of the photocatalytic properties of the $SiO_2@TiO_2$ core-shell particles [3].

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Sn-based materials applied as heterogeneous photocatalysts

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Heterogeneous photocatalysis is a process that utilizes the energy from incident radiation and the catalytic properties of semiconductor surface to carry out and/or accelerate certain chemical reactions, being studied for clean energy and environmental applications. Although TiO2-based materials are the most studied for photocatalytic applications, ternary oxide systems have been increasingly explored as photocatalysts, among them, spinel-based and perovskite-based photocatalysts. Our research group synthesizes and studies Sn-based photocatalysts of both classes of materials for the photodiscoloration and photodegradation of textile dyes: doped and undoped $A_2(Sn,Ti)O_4$ (A = Mg^{2+}, Zn^{2+}) and $ASnO_3$ (A = Ca^{2+}, Sr^{2+}, Ba^{2+}) solid solutions. The application of these materials in photocatalysis is still limited, but we have obtained interesting results in our experiments that stimulating the search for better understanding about the cristallyne structure of these materials. Alkaline earth stannates, $MSnO_3$, belong to the perovskite family with $A^{2+}B^{4+}O_3$ structure [1]. The substitution of the A^{2+} and/or B^{4+} sites might cause a modification of crystal structure, leading to delocalization of the charge carriers. The mobility of charge carriers influences in the photocatalytic activity because it affects the probability of charges reaching reaction sites on the photocatalyst surface. This effect can be even more pronounced for materials with AB_2O_4 structure, as for $Zn_2(Sn,Ti)O_4$ solid solutions, as in the inverse spinel structure, one-half of the A- ions are in the tetrahedral sites while the other half of the A-ions plus the B-ions occupy the octahedral sites [2]. Therefore, modification or doping with metal ions (e.g., rare earth and transition metals) has a considerable effect on the charge mobility and, for this reason, a more detailed knowlegde about the structural properties of these materials is very important, supporting the understanding on the mechanism of photocatalytic reactions, which is critically important to design and develop new photocatalytic materials. Rietveld refinement of well-defined X-ray Diffraction data may bring a better understanding about the crystalline structure and cation distribution in these systems, mainly within the spinel structure and the doped-perovskites. The influence of doping on the local order-disorder of the $[SnO_6]$, $[BaO_{12}]$, $[SrO_{12}]$ and $[CaO_{12}]$ complex clusters in perovskite systems and $[SnO_6]$, $[TiO_6]$, $[ZnO_6]$ and $[ZnO_4]$ clusters in spinels may be evaluated by Synchrotron X-ray Absorption Spectroscopy (XAS) techniques.

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Mesoporous silica nanoparticles as an alternative for Hodgkin lymphoma cells treatment

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Currently, chemotherapy is the main method used in the treatment of cancer and can be used alone or together with other forms of therapy.[1] However, it is known that conventional chemotherapy has certain limitations, among them, the low selectivity between diseased cells and healthy cells. On the other hand, nanotherapy has progressed rapidly in order to solve the problems presented by convencional chemotherapy.[2] Nanocarriers, for example, are biocompatible and biodegradable, and present several unique features such as high surface area, large pore volume and excellent physical and chemical stability. Besides, the encapsulation of drug in a nanoparticle can change their pharmacokinetics and distribution, increasing its effectiveness and reducing potential collateral effects. Among various drugs, doxorubicin (DOX) is one of the most effective and a common chemotherapeutic agent. However, once it intercalates into the DNA, it might compromises nucleic acids synthesis and leads cellular death.[3] Mesoporous silica nanoparticles have been used as drug delivery systems, due its ability to transport biologically active molecules. Besides, drug encapsulation into nanoparticles can change their pharmacokinetics and delivery increasing its effectiveness and reducing collateral effects. In this work, doxorubicin was encapsulated in silica nanoparticles through Stöber method[4]. Structures formed were characterized by small angle X-ray scattering (SAXS), Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA) and zeta potential techniques. Biological experiments are being conducted using Hodgkin lymphoma cells.

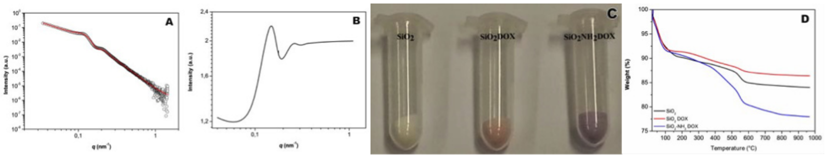

Figure 1: (a) SAXS pattern (open circles) obtained for mesoporous silica nanoparticles in detail, with corresponding fitting (solid line); (b) Structure factor obtained from SAXS fitting presented in Figure 1; (c) Photograph image of the as-synthesized silica nanoparticles without and with DOX; (D) TGA curves of synthesized nanoparticles. Black line: SiO_2; red line: SiO_2-DOX; and blue line: SiO_2-NH_2 DOX.

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Revealing the pressure-induced breakdown pathway in WS_2 nanotubes

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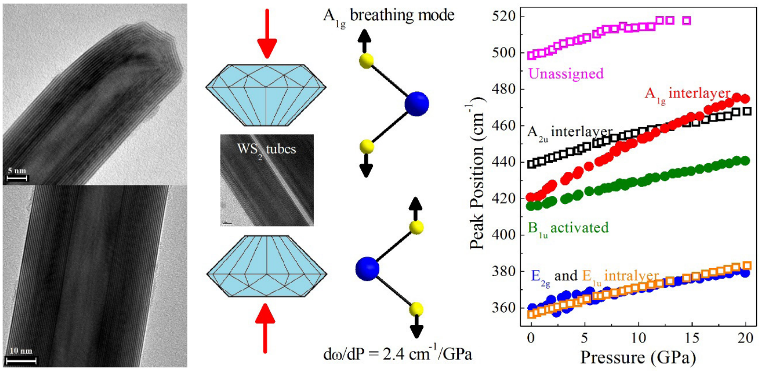
We report the high pressure infrared and Raman response of multi-walled WS_2 nanotubes up to 20 GPa in order to study the pressure-induced breakdown pathway. While most of the vibrational modes display similar compressibilities, the Raman active A_{1g} interlayer vibrational mode is almost twice as responsive, suggesting that the nanotube breakdown pathway proceeds through the interlayer breathing mode. Suppression of this vibration, for instance with a filler or a nanoscroll geometry, could prevent the breakdown and extend the range of solid state lubrication applications of these metal dichalcogenide nanotubes. An increasing infrared background is fit to a percolation model, indicating that the nanotubes display some conductivity although no metallic response is observed up to 20 GPa.



In-Situ Synchrotron SAXS Study of Self-Assembly Process at Low Temperature in Sol-Gel Derived Highly Ordered Titania Mesostructured Thin Films

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Highly ordered mesoporous thin films are typically produced through solvent evaporation and self-assembly process. In this method, the films are produced after evaporation of volatile species in as-made films. The final mesostructures is finely controlled by adjusting initial precursor compositions, aging condition and calcinations step. Recently, Oveisi et al. pointed out that the low aging temperature and humidity slowed down the hydrolysis and condensation reactions of alkoxide which favored the formation of highly ordered mesostructure [1,2]. In the present research we carefully investigated the order mesostructure formation in titania thin films at low temperature and humidity condition by using the cryogenic system and synchrotron radiation. This was done on a cooling stage which allows simulating the -20^{o}C aging temperature. In-situ GISAXS measurements during aging at -20^{o}C were successfully performed on as made film. The GISAXS patterns were shown that after 30 min aging, two different spots gradually appeared. These two out of plane intense spots correspond to (110) planes in a bcc mesostructure with Im3m symmetry. The basal spacing and the intensities of the (110) peaks were gradually increased, as the aging periods reached to 90 min. The most intense peak which was the highest ordered mesostructure appeared after 216 min aging. The significant changes in the evolution of GISAXS patterns are based on a self-assembly mechanism which is accompanied by the solvent evaporation. By increasing the aging time up to 216 min, position of the (110) plane spots in the out-of-plane gradually moved to the higher angle. In other words, the shrinkage of the structure was unidirectional; while no contraction parallel to the substrate was observed. The (110) spots became stronger with a large domain up to 216 min aging time. Based on the obtained results, it is considered that “low temperature and humidity” can avoid high rate reactions of hydrolysis and condensation of metal alkoxides. We clarified that an aging period of at least 4hrs is necessary to achieve the ordered titania mesostructure.

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Application of the automation techniques for X-ray imaging setups

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Current state of X-ray radiation sources allows investigation of dynamic processes. Dynamic processes studied at synchrotron radiation sources require fast frame rate from the detector system and its ability to keep with high flux imposed by the source of radiation, as well as high accuracy and reproducibility of the measurements. Also the present level of development of X-ray optics allows setting tasks that were impossible in the past. Application of focusing X-ray optics can increase the intensity and reduce the size of the focal spot of X-ray sources, such as e.g. betatrons, solving the fundamental problem of the device and increasing the range of its applications. It opens new imaging capabilities in medical diagnostic and in material analysis. A wide range of energies of secondary X-rays delivered by betatrons enables visualization techniques based on absorption contrast and phase contrast with X-ray diffraction gratings.

In light of mentioned above the automation of the process of the measurement becomes very important and non-trivial task. For the operation of the setup in the described investigations the automated processes of the installation and configuration should be organized, as well as interaction of system components in accordance to the type of the experiment and expected results, which have to be processed, analyzed and visualized also in automatic mode. Whereas the opportunity to control the experiment in real time with the capability of free programming of the algorithm should be also provided.

Development of the standardized framework will minimize human impact factor in measurements errors and will give to not enough experienced persons opportunity to adapt their ideas for current setup. In this purposes application of the automation techniques like fuzzy logic, model predictive control etc. allows to bring conducting measurements to the new level of authenticity.

Speciation of Chromium by X-Ray Absorption Near Edge Structure (XANES) in Sediments and Soils from Doce River Basin, Minas Gerais-Brazil

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The Doce river basin is located in the Southeast region of Brazil, with 86,715 km2 of drainage area. The population is approximately 3.6 million people and the agricultural is the predominant activity within the area covered by the basin. However, there are several important cities and industries with different activities and their anthropogenic actions are liable to generate contamination by several heavy metals, such as Cd, Cr, Ni, Ba, As, Co. In general, all heavy metals concentrations are above the Brazilian guideline environmental law.

Since the chromium is one of the most significant anthropogenic metal contaminants, this study aimed to define its speciation by X-Ray Absorption Near Edge Structure (XANES) in an attempt to predict their behavior in the Doce river basin. For this purpose, samples were collected along the main channel of the river and classified as stable upland soils, alluvial soils (present in floodplains), and sediments (from the riverbed).

The chromium contents were determined by x-ray fluorescence (XRF-SPECTRO XEPOS-AMETEK) and posteriorly some samples were selected and spatialized of all the sampled area for investigation by XANES. Cr K-edge XANES spectra were collected at beamline 11-2 the Stanford Synchrotron Radiation Laboratory - USA. The samples were ground to 200 mesh and diluted with BN (Boron Nitride), producing a pellet. These were placed in an aluminum sample holder with Kapton tape at an angle of 45° to the incident beam and collected fluorescence mode with Lytle detector. The Cr0.25Fe0.75(OH)3, Cr(OH)3 and Chromite (FeCr2O4) were the Cr standards analyzed and collected in transmission mode. Data processing was performed by ATHENA program.

The Cr concentrations found were between 108 to 390 µg/g in stable upland soils, alluvial soils, and sediments. These values are 40 % higher than the guideline value for this study area. The toxicity and transport behavior of Cr are strongly dependent by its valence. The most common oxidation states in the environment are hexavalent and trivalent. Cr(VI) has high solubility in natural waters, leading a high mobility in the environment and causing health human problems. Cr(VI) is a strong oxidant and considered carcinogenic by inhalation exposure. Differently, Cr(III) usually forms insoluble oxides and (oxy)hydroxides and, except in large amounts, is considered an essential nutrient for plants and humans. Analyzing the Cr K-edge XANES spectra we found that the risk of human contamination in this area by Cr is low, since it was showed only Cr(III) form in all compartments analyzed.

Data processing by Athena program was conducted in the form of Linear Combination Fitting-Manceau approach. The results showed that Cr0.25Fe0.75(OH)3 is the predominant form of Cr found in stable upland soils, indicating that it is adsorbed on the surface of the iron oxides. In alluvial soils and sediments its predominant form is the Chromite (FeCr2O4), causing by the elevated levels of this element as a primary mineral or even as isomorphic substitution in iron oxides.

Thus, we conclude that the Cr levels found in the Doce river basin is above the acceptable levels according to the Brazilian environmental law. However, it has been found in its trivalent oxidation state, which means it is not an immediate concern for humans.

Synthesis and characterization of chitosan/(ureasil–PEO hybrid) blend for drug delivery

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In the last years organic-inorganic hybrid materials have been the object of intensive studies due to their applications as carriers for controlled release of drugs [1-3]. Therefore, the objectives of this work were the synthesis and characterization of chitosan/(ureasil–polyethylene oxide hybrid) blends, and the study of their swelling and drug delivery behavior. The hybrids and the blends were prepared by the sol-gel route and characterized by infrared spectroscopy, differential scanning calorimetry, X-ray powder diffraction (XRPD) and small angle X-ray scattering (SAXS). Swelling and drug release processes in water were studied by gravimetric measurements of water uptake and UV-Vis absorption of the drug, respectively. The different characterization techniques revealed the formation of transparent, rubbery, flexible, water-insoluble, and low crystalline chitosan/(U-PEO hybrid) blends, which could easily dissolve pramoxine (used as a model drug). It was found that the combined addition of pramoxine and chitosan acted to decrease nanophase segregation between the organic and inorganic components of the hybrid matrix [1] and to increase the swelling degree. SAXS results showed that the average correlation distance between the adjacent siloxane nodes was increased by the water uptake [2] and this nanoscopic process showed three levels of swelling. The pseudo-first order rate constant for pramoxine release was essentially invariant with the amount of chitosan incorporated into the ureasil–PEO hybrid matrix, and the total amount of drug released decreased progressively with increasing chitosan content [1]. The results showed that the addition of chitosan provided a means of tailoring the amount of drug released at steady state equilibrium.

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Production, Characterization and Use of Sewage Sludge Biochar

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Sewage sludge is a semi-solid residue generated in large quantities, especially in developed urban centers. Its disposal faces significant environmental problems and therefore requires appropriate treatment and careful management. A viable alternative to reuse this residue is converting it to biochar through pyrolysis. Biochar, defined as any source of biomass that has undergone heat treatment at low levels or absence of oxygen, is gaining the attention of the political and scientific community because of its potential to improve soil productivity, remediate contaminated environments as a adsorbent and mitigate climate change [1,2]. Our project focuses on the production and characterization of sewage sludge biochar and its use as a heavy metal adsorbent, in soils from a Zn mining area in Brazil. Biochar yield decreased with increasing pyrolysis temperature, being 72 % of the original feedstock mass at 300 °C, 55 % at 500 °C and 50 % at 700 °C. The infrared spectra of the sludge and biochar samples revealed their complex chemical bond structure consisting of a mixture of mineral and organic matter. There was a slight decrease of total acidity (determined by Boehm's method) from 1.60 mmol g^{-1} at 300 °C to 1.20 mmol g^{-1} at 700 °C. The TG and DTG curves showed that sewage sludge exhibited three distinct zones during the combustion corresponding to moisture content released, volatile matter release and the combustion of fixed carbon. The SEM/EDS images revealed a solid mass of material with flakes or granules with an aspect of decomposed organic matter. According to semi-quantitative analysis (EDS) there was predominance of oxygen (30 %) and carbon (29%) followed by Fe (8.5 %), Si (8.3%), Al (6.7 %), Ca (6.0 %), Zn (3.3 %), Mg (1.5 %), P (1.3 %), Cl (1.3 %) and K (1.2 %). Minor proportions of S (0.8%) and Na (0.5%) were found. The biochar produced shall be used as a heavy metal adsorbent (eg. Cd, Pb and Zn) and tests in aqueous solution and in contaminated soils will be conducted. We will also apply activation methods in order to improve pore structure and area. Furthermore, extended X-ray absorption fine structure spectroscopy will help us understand mechanisms of heavy metals adsorption in biochar.

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Incubated epitaxy of GeTe on Si(111) studied by electron and x-ray diffraction

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GeTe is considered as a prime alternative to GeSbTe in phase change memory devices due to its better electrical contrast between the two phases, faster switching and longer data retentivity at higher temperatures. Being a binary material and analogous to GeSbTe in terms of switching properties, it is widely studied to understand the switching mechanism of GeSbTe based ternary alloys. Molecular beam epitaxy of GeTe is performed on highly lattice mismatched Si(111) and Si(001) substrates. GeTe grows along [111] direction irrespective of whether the substrate is (001) or (111) oriented. Besides RHEED images at the onset of GeTe growth on Si(111) indicate an initial amorphous-to-crystalline transition during the first few nanometers of growth. Azimuthal RHEED images taken during the nucleation stage indicate a weak four fold surface symmetry before it turns to six fold symmetry at the onset of crystalline transition. *In-vivo* x-ray diffraction studies performed during the initial stages of growth indicate a [001] oriented growth before the film grows along [111] direction. Extensive x-ray diffraction analyses show that the film is rhombohedrally distorted, with the distortion along [111] direction. In-plane azimuthal x-ray diffraction scans show the presence of rotational domains with a considerable twist (~14°) in the epitaxial layers, which is structured into five intensity maxima.

Physicochemical and structural characterization of lipids blends as a new strategy for gene delivery.

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In this work we report the preparation and characterization of cationic liposomes and Langmuir monolayers of the lipid blend EPC/DOTAP/DOPE (2:1:1 mol %) associated with hyaluronic acid (HA) of 16 kDa, for the development of new strategies for delivery systems in gene therapy. The goal was to determine the main parameters of the association between the lipid blend and the HA aiming the control of physical-chemical and structural properties of the system. DLS and zeta potential studies for liposomal dispersion for low concentration of HA between 0.25-3% of HA (m/m), showed an initial phase of equal averaged-sizes as pure extruded liposomes; and positive surface electric charge as the cationic liposomes. For quantities between 3-20 % of HA (m/m), occurs an inversion of surface charge and formation of large agglomerates. From 20% of HA, the size decreases until reach a concentration of about 80 % of HA (m/m), showing a phase of perfect combination and complete dispersion of liposomes, considered propitious for application in gene carriers systems for gene therapy. All the phases of HA combination were observed by Cryo-TEM [1]. In addition, we performed studies on HA absorption in Langmuir's monolayers for every lipid in the blend, proving that the HA association in the interface occurs mainly by the electrostatic interaction of HA with DOTAP.

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Application of synchrotron-based techniques in investigations of archaeological biomarkers: microenvironmental effects on heme group preservation

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The knowledge and preservation of cultural heritage objects is of great importance because they represent cultural, historical and technological developments of societies. In such a context, these objects need to be preserved. Considering the physicochemical complexity of these systems and that both chemical and physical characterization is necessary, the use of scientific tools and methodologies is essential.

For archaeology, the use of scientific instruments and knowledge on physical and chemical characterization of objects defines what is known as archaeometry. Investigations in this field aim at correlating the chemical composition of objects, and of their environments, with past human activities, rescuing historical, cultural and technological information. Although the presence of inorganic compounds in archaeological objects is usually related to past human activities and to environmental exposure/contamination, organic and biological molecules can usually reveal much more information. However, organic matter is commonly present as residues, because of their high degradation susceptibility. The investigation of these organic residues in archaeology is very important and recognized and, when these materials result in information about human activities, they are called as archaeological biomarkers. [1] Examples of biomarkers are DNA, blood (specially through the heme group), resins, amino acids, peptides, waxes, animal and vegetable fats, oils, proteins and food remains. Such biomarkers, can be degraded in processes associated with human activities, such as cooking or heating for technological application, or by their interaction with the archaeological microenvironments, being affected by variables such as temperature, relative humidity, acidity, pressure and presence of organic or inorganic matter. Considering that they are usually found in their non-original forms even if good preservation conditions are present, the understanding of the mechanisms of degradation in different conditions is necessary to a better understand of the original compositions.

The characterization techniques to be used in works of art (including the archaeological objects) should be, ideally, non-destructive and non-invasive, and present high lateral resolution. It is also desirable the use of complementary techniques, since the samples are chemically complex systems. In such context, synchrotron based-techniques are being increasingly employed in cultural heritage investigations in the last years, [2] because they can be non-destructive or invasive, can present lateral resolution in the range of microns or sub-microns and present high energy tunability (from the far infrared region up to hard X-rays). In addition, synchrotron sources are brighter than conventional ones, with techniques like XAS (X-ray Absorption Spectroscopy) [2] being able to reveal important information about the chemical composition of artifacts and of their degradation products. Taking into account the above exposed aspects, this abstract aims to present and discuss our ongoing project on the application of synchrotron-based techniques to investigate the effect of archaeological microenvironments (inorganic matrices, temperature, relative humidity and pressure) on the degradation of solid heme group. The project is being developed at LNLS and USP and will consider the use of other well-established techniques in archaeometry, such as infrared absorption and Raman spectroscopies.

Heme group is a porphyrin present in blood and is related to important information about ancient and historical materials. [3-6] Considering that this biomarker is of interest to others fields of knowledge, the results to be obtained should be extended at least to paleontology and astrobiology. [7,8]

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Ammonia Monohydrate at High Pressure

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Knowing the properties of H_2O, NH_3 and their mixtures under high pressure and temperature is important for planetary science because these H-bonded ices are present in Jovian planets and their satellites under a wide range of pressure (P) and temperature (T) conditions. The high P-T properties of the pure ice compounds have been the focus of many investigations, which have revealed a rich polymorphism. In particular, our group has recently shown the existence of superionic and ionic phases of ammonia [1,2], which had been previously predicted by first principles calculations [3,4]. In these phases, proton transfers between molecules give rises to ionic species NH_4^+ and NH_2^-, which may be relevant to explain the magnetic fields of Neptune or Uranus. By contrast with the pure components, the properties of (H_2O, NH_3) mixtures under extreme P-T conditions have been much less explored although these systems are possibly more relevant for planetary physics.

This presentation will focus on the properties of the ammonia monohydrate (AMH) solid compound, with stoechiometry 1 NH_3:1 H_2O. Experimental high-pressure studies on these systems have been mostly limited to P< 10 GPa and T<300 K and reveal a rich polymorphism as at least 6 phases are reported. The known phases are all molecular and present heteronuclear O...H-N and N-H...O hydrogen bonds, as encountered in more complex macromolecules such as DNA. Nevertheless, a recent theoretical study [6] has suggested that AMH transforms into an ionic solid composed of NH_4^+ and OH^- ions, in a similar fashion as the self-ionization observed in pure ammonia [2], but at much lower pressures (10 GPa instead of 150 GPa), thus much easier to reach in experiments. To check this surprising prediction, we have performed the first infrared absorption studies of AMH up to 40 GPa at 300 K and 100 K on SMIS beamline and X-ray diffraction experiments over a wide range of pressure and temperature on PSICHE beamline and on ID 27 at ESRF. The molecular/ionic phase transition is indeed observed, as evidenced by the appearance of vibrational modes from NH_4^+ and OH^- species, but the observed structure is not compatible with the predicted one. We will discuss our results in this presentation.

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Nanostructured Molybdenum Carbides as Catalysts for Biomass Valorization

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In the last decade, there has been an increasing interest in using low cost transition metal carbides (TMCs) as high performance catalysts for valuable reactions such as conversion of biomass platform molecules and hydrogen production from water splitting, among others. Molybdenum carbides (Mo_2C) have received special attention as they present similar or comparable catalytic activities as those of the platinum group metals [1].

It is well known that the catalytic properties of Mo_2C depend on their surface area and structure, which are closely associated with their method of synthesis [1]. Typical synthetic strategies usually produce carbides with irregular shapes and random size distribution. The development of nanostructures Mo_2C has become a main topic in materials science since they have shown interesting and promising behaviors in catalysis compared to their corresponding grain-sized materials [2]. My current research is focused on the synthesis and characterization of nanostructured Mo_2C base materials and their application as catalysts for sustainable process.

The first study concerns the effect of the morphology and size of unsupported molybdenum carbides (β-Mo_2C) on the selective hydrogenation of levulinic acid (LA) to γ-valerolactone (GVL). Unsupported β-Mo_2C carbides with different morphologies were synthesized according to different approaches i) using multiwalled carbon nanotubes (CNT) as template and; ii) using 1D nanostructured α-MoO_3 as precursor. The materials were active towards LA hydrogenation in the aqueous phase, producing GVL very selectively and in high yields. For the β-Mo_2C synthesized from the nanostructured α-MoO_3 (Fig. 1 a, b) a more efficient catalyst with conversion and selectivity values greater than 90 % was obtained, highlighting the catalytic benefits associated with the control of morphology and size in unsupported β-Mo_2C [3].

The second study is related to supported Mo_2C nanoparticles. Recently, Mai *et al*. [4] reported that Mo_2C confined nanoparticles within carbon nanotubes result as an efficient catalyst for biomass conversion. This study is extended to account for the confinement effect of Mo_2C nanoparticles supported on mesoporous hollow carbon nanospheres (HCSs). We synthesized the HCSs by a modified Stöber method using silica as template [5]. The SEM images confirm the formation of the HCSs (Fig. 1 c) with diameters between 300-400 nm. The N_2 adsorption desorption isotherms (Fig. 1 d) exhibit typical type IV hysteresis, indicative of the presence of mesopores, with pore size distribution centered at around 5 nm and a BET specific surface area of 300 m^2/g. Different parameters are under study for supporting Mo_2C nanoparticles over these materials. The resulting Mo_2C/HCSs catalyst seems to act as a promising alternative for biomass valorization.

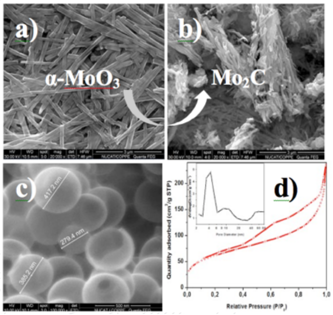

Figure 1. SEM images of nanostructure
a) MoO_3 and
b) Mo_2C
c) SEM images of hollow carbon nanospheres (HCSs) and
d) N_2 adsorption isotherm and pore size distribution of HCSs.

Humidity Dependent Hydroxylation of ZnO Single Crystals

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The interaction of water with metal oxides plays an important role in materials science, catalysis, fuel cells, corrosion of building materials, mineral weathering, and environmental chemistry [1]. When trying to understand metal oxide interfaces under ambient conditions, water becomes important. Ambient pressure X-ray photoelectron spectroscopy (APXPS) has been used as a powerful probe to measure the detail interactions of water vapor with various metal oxide surfaces under ambient conditions, including TiO2(110), SiO2, Cu2O, Al2O3, FeO, BaCeY-oxide, LaCoO3(001), iridium oxide, cerium oxide, GeO2, Fe2O3(0001), Fe3O4(001), and MgO. For our future research project we wish to investigate ZnO, which is a heavily investigated substrate as a model catalyst, but remains largely unexplored under ambient water vapor conditions using APXPS. This project will be continuation of our initial APXPS examination of water reaction with single crystalline, non-polar ZnO (10-10) conducted at Brookhaven National Laboratory (BNL) National Synchrotron Light Source (NSLS) beamline X1A1 [2].

For the research proposed, we wish to determine the relative humidity at which different ZnO crystals hydroxylate and compare this to our previous results. Such results would have significant implications for ZnO particle catalysts which are made up of various different terminations. The results of these ZnO studies will allow for the extraction of the enthalpy and entropy of hydroxylation, and desorption frequency factor for OH recombination.

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Structural Properties of urethane/urea Elastomers and Ferrogels

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Elastomers are amorphous cross-linked polymer networks existing above their glass transition temperature. The most important property of such materials are their high elasticity, i.e., the capability of recovering their original shape without permanent deformation after being stretched to great extents.

The inclusion of magnetic nanoparticles into elastomeric polymer networks produces materials that combine the high elasticity of elastomers with the high magnetic susceptibility of these nanoparticles, i.e., it creates a coupling between the magnetization and the elastic response. These materials are named ferrogels and they have promising applications as sensors, actuators, artificial muscles and so on.

Particularly, urethane/urea elastomers consist of small hard segments formed by urethane and urea groups, and soft segments formed by long chains, ordinarily of a polyether or polyester. The molecular structure and subsequent macroscopic properties of such elastomers are highly dependent on the type and arrangement of these hard and soft segments in the network. Urethane/urea elastomers with two soft segments, polypropylene oxide (PU) and polybutadiene (PBDO), were primarily proposed as an optimization of elastomeric membranes for pervaporation [1], but their ease of synthesis and versatility in the formation of structures made them a good choice for further research.

These urethane/urea elastomers of PU/PBDO were used in the construction of different macroscopic objects such as freestanding membranes, microspheres and cylindrical fibers, as well as in the Janus versions of these objects, with one half of the surface with a wrinkled pattern and the other half with a flat pattern [2,3]. Also, membranes of urethane/urea ferrogels (PU/PBDO) with Fe_3O_4 nanoparticles embedded into the polymer network were produced and studied [4].

Some recent results on structural properties of membranes of urethane/urea elastomers and ferrogels of PU/PBDO will be presented and, possibly, also the properties of other macroscopic objects made with these ferrogels. Results of microscopic structures and topographical features of the membranes will be highlighted, obtained with different experimental techniques such as small-angle X-ray scattering, transmission electron microscopy, Fourier transform infrared spectroscopy and scanning electron microscopy.

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Cretaceous Floras from Pernambuco State

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The Cretaceous was a complex geological period with significant environmental changes that influenced the life in continents and oceans. Spanning from approximately 145 to 66 million years, the Cretaceous witnessed geological events with no analogues today. Elevated global temperatures and atmospheric CO_2 levels, rising sea levels, ocean anoxia and increased volcanic activity, caused changes in ecosystems, with diversifications and extinctions of organisms during the whole period, specially at the end of it. In terrestrial ecosystems of the beginning of the Cretaceous, dominant groups of plants were ferns and gymnosperms, but at the end of the period, the flora becomes dominated by angiosperms. Despite the amount of existing studies on Cretaceous floras, no one knows for sure the reason for this change, neither the mechanism nor the place where the angiosperms began to turn into the dominant group of plants until today. In addition, there is a lack of sampling in the tropics, currently holding the largest plant diversity of the planet and frequently thought as the center of origin for the flowering plants. The paleogeographic position of Pernambuco State, in the Cretaceous tropics, and the privilege of having a fossil record of floras at different points during the period, allows the analysis of the evolution of plants across this important time interval. The studied paleofloras occurs in: Late Jurassic to Early Cretaceous, Sergi Formation in Jatobá Basin; Early Cretaceous Marizal Formation in Mirandiba Basin; Early to Late Cretaceous Romualdo Formation in the Araripe Basin; Late Cretaceous shales associated with Ipojuca Magmatic Suite in Pernambuco Basin; Late Cretaceous Gramame Formation of Paraiba Basin. By systematic collection and application of classical paleobotanical techniques and more refined as Scanning Electronic Microscopy and Computed Microtomography, it is expected to achieve a significant advance in knowledge of the components of Brazilian Cretaceous paleofloras. Results will contribute to the understanding of plant evolution and terrestrial ecosystems from the tropics viewpoint, little known in the paleontological global scenario. It is also intended to encourage research in paleobotany in the Pernambuco State and communicate results to scientific community and enthusiasts.

Photodegradation of Astrophysical Ices induced by Synchrotron Radiation

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Acetonitrile (CH_3CN), formamide ($HCONH_2$) and acetone (CH_3COCH_3) are relevant astrophysical molecules. They have been identified by their radiofrequency emission toward Sagitarius B2 molecular cloud, a chemically rich region of gas and dust in the vicinities of the Milky Way core. Acetonitrile was also detected in the Kohoutek comet, as well as formamide was found to be present in Hale-Bopp comet and tentatively identified in young stellar objects, such as W33A and NGC 7538 IRS9. All these environments are exposed to ionizing agents, in particular photons, electrons and cosmic rays, causing fragmentation and further desorption of neutral and ionic species, leading to the formation of more complex molecules. In order to simulate the astrophysical reality under laboratory conditions, astrophysical ice analogs of acetonitrile, formamide and acetone were condensed at 10 K in situ inside and ultra-high vacuum chamber. These ices were exposed to zero order synchrotron radiation (non-monochromatic) in the Spherical Grating Monochromator beamline (SGM) of the Laboratório Nacional de Luz Síncrotron (LNLS). The ice degradation was monitored by Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy at the nitrogen and oxygen K-edge. Destruction cross-sections were derived for each molecule as a function of the photon fluence.

Exploiting the possibilities of new X-ray imaging techniques

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X-ray imaging is a rapidly developing area were the boundaries for what is possible is constantly moving. There are many different types of imaging techniques and these are applicable in many branches of science. These techniques are very attractive to the medical-, food- and material science and industry, to mention a few. It is possible to acquire high quality 3D tomograms with nano-scale resolution using methods such as X-ray ptychography. X-ray ptychographic tomography is a novel synchrotron-based 3D imaging technique, which can be used on a large variety of samples from food emulsions to rocks. Another developing method is propagation base phase contrast tomography, which is ideal for investigation of soft tissues where it can be difficult to get sufficient contrast using normal absorption tomography.

In the x-ray imaging group at the Niels Bohr Institute, we work with such techniques to push the boundaries for what is possible to image. Here I present some results from some measurements preformed at Swiss Light Source using these specific techniques. Specifically propagation based phase contrast tomography on chicken meat breast and X-ray ptychographic tomography used to image the structure of an emulsion solution.

Influence of Pt in Ge/HfO$_2$/Pt Stacks submitted to Post Deposition Annealing

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The search for new materials in the microelectronic industry is mandatory in order to continue device evolution [1]. High mobility, low band gap, and adaptability for current industrial processes are advantages of germanium (Ge) as an alternative material to substitute silicon (Si) on MOSFETs fabrication [2,3,4]. Ge oxide can be thermally grown, leading to good GeO$_2$/Ge interface quality, as is historically made with Si. [5,6]. However, GeO$_2$ is water soluble and the Ge/GeO$_2$ interface is thermally unstable [7]. Therefore, dielectric deposition seems to be an alternative. Nevertheless using atomic layer deposition, a thin Ge oxide interlayer is formed [8]. Usually, post deposition annealing (PDA) is performed in order to heal defects and to improve interface quality in MOS structures. In the present work, oxygen incorporation on metal oxide semiconductor structures was investigated. Pt/HfO$_2$/Ge and Pt/HfO$_2$/Si were fabricated using magnetron sputtering. PDA was performed in an ^{18}O isotopically enriched atmosphere. The incorporation of this isotope was determined by NRA and NRP measurements, in order to investigate the role of Pt in the incorporation process. Pt was shown to act as a dissociation agent of O$_2$, creating oxygenic species able to diffuse through HfO$_2$ and to react with the Ge substrate.

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ZnO semiconductor thin films grown by electrochemical deposition in deep eutectic solvent

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Solar energy represents the most abundant source of renewable energy [1]. In recently year, greatly advance has been made in development of photovoltaic devices. In particular, thin films semiconductor has shown great interest on this research field [2]. Zinc oxide is an n-type semiconductor material with wurtzite crystalline structure having a wide band gap (3.2-3.4 eV) at room temperature [3]. Zinc oxide thin film is widely used in piezoelectric transducers, light emitting devices, photosensors and photovoltaic cells [4]. In this study, zinc oxide thin films will be electrodeposition in eutectic-based ionic liquid. The experiments will be performed in a three electrode electrochemical cell with fluoride doped tin oxide (FTO) as a working electrode, a Pt sheet as the counter electrode and Ag wire as the pseudo-reference. The electrodepositions will be carried out on a geometric surface of ~1 cm^2. The electrochemical bath will be composed of $ZnCl_2$ solution in choline chloride-ethylene glycol (1:2) deep eutectic solvent, saturated with O_2. Cyclic voltammetry scans will be performed at a scan rate of 50 mVs^{-1}. The experiments will be performed at constant potential at -1.2 and -1.6 V and under a constant current density a 1.5 and 3.0 $mAcm^{-2}$, at room temperature and 60, 100 and 150 °C. The morphology of the thin films will be investigated using a Quanta FEI® field emission gun (FEG) microscope equipped with Oxford® device for chemical analysis by energy dispersive spectroscopy (EDS). The crystalline structure will be analyzed with a Panalytical® X´pert Pro X-ray diffractometer using Cu radiation. In order to investigate the semiconductor behavior and analyze light emission properties of samples the optical transmittance and photoluminescence will perform. We expect in the end, found the best morphologies for photovoltaic applications.

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Longitudinal Beam Profile Measurements in Linac4 Commissioning

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Linac4, the future 160 MeV H$^-$ injector to the CERN Proton Synchrotron Booster, is presently under construction at CERN as a central step of the planned upgrade of the LHC injectors. The Linac front-end, composed of a 45 keV ion source, a Low Energy Beam Transport (LEBT), a 352.2 MHz Radio Frequency Quadrupole (RFQ) and a Medium Energy Beam Transport (MEBT) housing a beam chopper, has been installed and commissioned. Precise measurements of the longitudinal micro bunch profiles of ion beams were possible with the help of a Bunch Shape Monitor (BSM) developed at INR Moscow. These were crucial for the successful commissioning of the three RF buncher cavities mounted along the MEBT and well complemented with higher precision the information provided in parallel by spectrometer measurements.

FTIR and SAXS Investigations and Structural Characterization of Spicules from Natural Sponges

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Superior properties of the nanoscale-structured materials and their ease of use are one of the most important benefits of nanotechnology. Such materials started to be achieved artificially by nanotechnology are actually naturally for thousands of years in nature. One of these biological materials containing nano-formations which have high crystallinity and can produce natural silicon is also natural sea sponge [1]. Because of their biotechnological potential, sponges are very valuable to the chemists, physicist and pharmacologists[2]. Structures of sponges have been discovered with cytotoxic, antifouling, antitumoral, antibiotic, antiviral, cytoprotective, enzyme-inhibitory, anti-inflammatory and anti- Alzheimer applications [3]. Sponges can inspire new materials with biomimetic approach [4].

Sponges, is supported by fine glass needle-like structures forming the skeleton which called spicules. Spicules help to sponge to hold the sea surface. Sponges are classified according to Si and Ca content of spicules.

In our study, sponges which have spicule skeleton were obtained from the Turkey. Conventional Small Angle X-ray Scattering (SAXS), Fourier Transform Infrared Spectroscopy (FTIR) techniques were used to obtain pre-structural (micro and nano scales) information .

We are planning to do experiments for further analysis using beamlines 16 LNLS.

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Synthesis and characterization of nanocomposite vanadium oxide with gold nanoparticles stabilized in dendrimers

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Unidimensional materials (1D) as nanotubes, nanowires and nanowhiskers have been the focus of intense study for application in sensors, optical elements for optoelectronics, converters for nonlinear optics, energy storage and interconversion, etc [1]. Can be found in the literature, several types of nanotubes highlighting of carbon nanotubes, and transition metal oxide nanotubes. Among the nanotubes of transition metal oxides stands out vanadium oxide nanotubes [2,3]. The synthesis of vanadium oxide nanotubes occurs from the sol gel route and subsequent hydrothermal treatment for 7 days at 180 °C temperature. When nanocomposites vanadium oxide and aliphatic amines are subjected to the hydrothermal treatment, the alcohol used to form the metal alkoxide promotes partial reduction of the oxide, V^{5+} to V^{4+} which, in turn, causes to the protonation of the grouping amine present in alkylamine molecule. The hydrothermal treatment allows the compensation of dangling bonds from peripheral structure in the vanadium oxide nanocomposite. This compensation is reflected from the winding structure from the forming edges "(nano) rolls" vanadium oxide molecules separated by alkylamines [2].

Dendrimers (DEN) possess all the characteristics of a stabilizing agent and have been very applied in the synthesis of metal nanoparticles. Furthermore dendrimers have also been used to introduce new properties and functionalities to carbon nanotubes [4]. In this contest our work aims to study the behavior of unidimencionais nanostructured materials synthesized from vanadium oxide nanotubes and gold nanoparticles stabilized sterically in dendrimers. In this study was investigated the unprecedented interaction between dendrimer-Au with vanadium oxide nanotubes using cationic exchange methodologies. After the synthesis process the materials were characterized using spectrophotometry techniques in the UV-Vis region, X-ray diffraction (XRD), scanning electron microscopy (SEM) transmission electron microscopy (TEM), Fourier transform infrared (FTIR), and scanning electron microscopy (SEM), photoelectron spectroscopy excited by X-rays (XPS).

Finally the characterization results show that the use of dendrimer-Au keep the tubular morphology, in addition has no observed displacement of the interlayer region from vanadium oxide, indicating no exchange occurs between dendrimer-Au by the template present between the layers of nanotubes. Therefore the results have enabled identification of a tubular nanostructured material containing gold nanoparticles with sizes around 3 nm on the surface of these nanotubes.

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Spectroscopic characterization of the interface semiconductor/active layer in sensors based on DNA

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DNA sensors are high sensitivity and selectivity for the detection of pathogenic and genetic diseases by binding to target DNA strands that are related to the disease. The adsorption of components DNA has relevance in understanding surface interactions in biosensors based on TiO_2 [1, 2,]. In order to determine which DNA is more suitable as biologically active layer for biosensors was used X-ray photoelectron spectroscopy (XPS), near-edge X-ray absorption fine structure spectroscopy (NEXAFS). As the biologically active layer were employed the DNA of three kinds of different extraction methods, that is plasmid, genomic and PCR and all were anchored on the nanostructured semiconductor layer. The NEXAFS experiments were carried out in the SGM beam line (250-1000 eV) at the LNLS, Campinas-SP. The XPS spectra were obtained at the LaQuiS-IQ, UFRJ. NEXAFS and XPS spectra were obtained in the edges 1sC, 1sN, 1sO, 2pTi and 2sP before and after the anchorage the active layer for each type of DNA (genomic DNA/TiO_2, plasmid DNA/TiO_2 and PCR/TiO_2). The angle of incidence of the beam with the sample normal was about 90° and NEXAFS spectra were obtained mode TEY. For genomic DNA/TiO_2, all NEXAFS spectra showed a low intensities and a slight chemical shifts for low energies in relation to others samples. The plasmid DNA/TiO_2 and PCR/TiO_2 are very similar showing slight differences. In the XPS spectra, genomic DNA presented an opposite behavior, high intensities and shifts to higher energies in relation to others samples. These results indicate a resistive character in charge mobility in the sample genomic DNA/TiO_2. We attribute this character resistive the presence of histone proteins in structure genomic DNA even after the removal treatment. A comparative study between the different kinds of anchored DNA was performed to deepen in to the mechanisms of anchoring of the biologically active layers on semiconductor substrate through the NEXAFS and XPS. We conclude that the genomic DNA is little suitable for biologically active layer in electrochemical sensors compared to the other DNA, as plasmid and PCR.

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Hydrogels Materials based on Short Peptides for encapsulation of biomolecules

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There is a strong need to develop biomaterials for applications in diagnosis and therapeutics. In this scenery, the immobilization of biomolecules has an intense research activity because encapsulation improves the stability of proteins as enzymes, antigens and others, which would open the a large number of applications as tissue engineering[1], drug deliver, enrironmental applications besides develop a diagnostic biosensors in the near future when creates biological-responsive hydrogels capable of recognizing specifically antibodies or antigens. This addresses major challenges in the synthesis of biocompatible and biomimetic materials which to date have limited responsiveness. Two different hidrogels were produced using peptides in the sequence of Fmoc-diphenylalanine (FmocFF or FmocPhePhe)[2] and Fmoc-cysteinediphenylalanine (FmocCFF or FmocCysPhePhe). The aim of these materials is encapsulate of biomolecules as antigens for leishmaniasis disease, that it is a tropical problem present in Brazil. These hydrogels were characterized on the surface and porous structure using electron microscope technique prepared using frozen samples. The swelling ratio was studied for both hydrogel produced using liofilization process and weight difference. The encapsulation system was studied using infrared spectroscopy (FTIR) and RAMAN spectroscopy. The hydrogel activity was applied for the encapsulation of leishmaniasis antigens. The antigens were extracted from promastigotes of L. infantum Promastigotes, which were harvested from an LIT (Liver Infusion Tryptose) medium[3]. It is expected that the systems and concepts developed will have much broader potential in the creation of new diagnostic and therapeutic systems towards other conditions involving proteases including immune diseases, cancer and other diseases.

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Manganese is a key element for cancer cell migration and metastasis

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The metastatic disease is one of the main consequences of tumor progression, being responsible for most cancer-related deaths worldwide [1]. The sequence of events that lead to the formation of a metastasis start with the acquisition of an invasive phenotype by cells in the primary tumor; this happens in parallel to the secretion of tumor-derived products into the bloodstream. These products will regulate the formation of tumor-promoting microenvironments in the organism, called premetastatic niches, which the invasive cells will subsequently reach and populate [2]. In order to perform all these steps, tumor cells need efficient mechanisms of migration into the premetastatic niches. Invasive cells are able to migrate, leaving the primary tumor, reaching these niches and colonizing healthy tissue. Migration via integrin activation by the cell surface proteoglycan syndecan-1 has been linked to tumor progression [3]. Integrins are cation-dependent molecules, whereas manganese promotes integrin activation by high affinity binding [4]. Our work has revealed that different tumor cell lines respond to manganese exposure by migrating faster compared to control conditions, and this activity is accompanied by higher occurrence of syndecan-1, a molecule that carries heparan sulfate (HS) chains. *In vitro* and X ray fluorescence analyses (D09B beamline, LNLS) revealed that HS analogues are able to capture manganese and revert its migration-promoting effects on tumor cells. Therefore, we hypothesize that HS chains themselves and their analogues are able to bind free manganese. Manganese-bound syndecan-1 interacts with integrins which, in turn, become highly active and promote cell migration. On the other hand, soluble HS analogues disrupt this interaction and compete with tumor cells for free manganese. A mouse model of spontaneous metastasis revealed that high-syndecan-1 cells occur in clusters within the primary tumor and metastatic livers, and in parallel we were able to detect areas of high manganese concentration, usually near high-syndecan-1 cell clusters. High manganese areas were mapped between 0 to 5 weeks of tumor progression and we were able to detect a consistent rise in manganese within the primary tumor, while metastatic livers were only different from controls at the fifth week, when metastases become detectable. Manganese was also detected in the bloodstream and we observed a drastic rise in manganese blood concentration at week 5, while other elements, such as iron and calcium, remained unchanged. This phenomenon indicates a possible blood manganese rise caused by the primary tumor and the premetastatic niches seeded in the organism. Finally, colon adenocarcinoma patient samples from Hospital Naval Marcílio Dias (HNMD, Rio de Janeiro) were analyzed for manganese presence. Our preliminary data revealed that manganese could be detected within the primary tumor, tumor surrounding areas and metastases, but not in tumor-free, -distant areas. We conclude that manganese appears to be a key factor in tumor development, especially involved in tumor metastasis. Our perspectives include further experiments to clarify manganese role in premetastatic niche formation and the design of possible mechanisms of metastasis inhibition via manganese chelation by HS analogues.

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Modeling Depth Resolved XRF data to study Semiconductor-Oxide Thin Films doped with transition metals ions

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Grazing Incidence X-Ray Fluorescence (GI-XRF) technique is a powerful tool for the characterization of depth profile concentrations in multilayered samples. A modeling program called ANDEN has been developed for simulating GI-XRF data for layered thin films [1]. ANDEN was used as one of the tools to study the dependence of dopants distribution with magnetic behavior in Diluted Magnetic Semiconductors (DMS). These new kind of materials attract attention because of their potential applications in spintronics, once they showed ferromagnetic properties at room temperature [2]. Co-doped TiO2 and SnO2 thin films were grown on Si, LaAlO3 (LAO) and SrTiO3 (STO) substrates using both DC/RF Sputtering and Pulsed Laser Deposition (PLD). Combined GI-XRF and X-ray Reflectivity (XRR) were used to study cobalt depth profile within the films. In addition, magnetic properties of these films were also studied using complementary techniques such as superconducting quantum interference device (SQUID) and X-ray Magnetic Circular Dichroism (XMCD). GIXRF, XRR and XMCD measurements were performed at the Brazilian Synchrotron Light Laboratory in Campinas, Brazil. In this work, an overall description of the ANDEN program as well as the main results about the behavior of Co in semiconductor oxide thin film, will be given.

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Gas Sensor Performance of SnO_2, SnO and Sn_3O_4 Nanobelts Synthesized by Carbothermal Reduction Method

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The development of new chemical sensors made from semiconductor nanostructures with optimized morphologies has attracted great interest in recent years. It is expected that these devices may be able to detect pollutant gases at ppm, and even ppb levels, with high sensitivity, stability, selectivity and response speed in order to satisfy a wide range of requirements in the safety, health, environment and energy conservation areas [1,2]. While SnO_2 is the most studied and best-known gas sensing material, the gas sensor properties of tin oxides with unusual stoichiometries (e.g. SnO and Sn_3O_4) have very recently been reported [3,4]. The delay in examination of these other tin oxide phases is not surprising given the difficulty in synthesizing them and their thermal instability at high temperatures. Due to the initial attractive sensor response reported for both SnO and Sn_3O_4, the gas sensor performance of these new alternative tin oxide based materials merit closer examination, particularly in comparison to the response of the standard SnO_2 sensor material. In this work, a comparative study of the gas sensor performance of tin oxide nanobelts with different stoichiometries (SnO_2, SnO and Sn_3O_4), synthesized by a carbothermal reduction method, is presented. The influence of the surface modification of these tin oxide nanostructures by adding metallic nanoparticles (Pt, Pd and Ag) on their gas sensor response, is also reported. Analyzes by X- ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) showed that by controlling the synthesis conditions it is possible to obtain structures in different tin oxidation states. The results also indicated that the nanobelts are single-crystalline with relatively uniform widths along the growth direction and lengths of the order of dozens of microns or even millimeters. Additionally, SnO_2, SnO and Sn_3O_4 nanobelts were found to grow in the tetragonal, orthorhombic and triclinic structures, respectively. Gas sensor measurements showed that the sensor based on Sn_3O_4 nanobelts exhibits the highest sensor response to 50 ppm NO_2 at 200 °C with an approximately 155-fold increase in electrical resistance. Moreover, at this operating temperature, Sn_3O_4 nanobelts were found to display the highest selectivity to NO_2 relative to CO while SnO nanobelts exhibited the highest selectivity to NO_2 relative to H_2 and CH_4. On the other hand, the decorated nanostructures presented high sensitivity for H_2 or CO depending on the operating conditions. It is discussed the unusual surface electronic structure of these novel tin oxides that may contribute to their enhanced sensitivity. Overall, these results suggest that tin oxide semiconducting nanomaterials, with the unusual oxidation states of SnO and Sn_3O_4, show great promise as alternatives to SnO_2 for use in high performance gas sensor devices.

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Genesis of gold nanoparticles: nucleation, growth and stabilisation studies.

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Synthesis of metallic nanoparticles is an area of ever-growing interest for the scientific community. Colloidal gold solutions are very fascinating systems due to their biocompatibility and the possibility to functionalise the surface of the nanoparticles with various biological molecules. This ensures original applications related to gold nanoparticles in various fields such as biology [1] and for example, curing diseases [2] but also catalysis. A route of synthesis which has been popular for a long time uses citrate as the reducing agent and the gold salt $HAuCl_4$ as the precursor in water [3].

Room-temperature ionic liquids are attracting much interest in many fields of chemistry and industry, due to their potential as a "green" recyclable alternative to the traditional organic solvents. They are nonvolatile, nonflamability and have high ionic conductivity. Nevertheless, the development and applicability of such properties rely on the ability to produce stable monodisperse nanoparticles of specific shape and chemical compositions. The actual mechanisms of nanoparticle formation and growth often remain unclear due to limited accessibility to *in situ* time-resolved information about the evolutions of precursor speciation and particle size. There is thus a very strong need for a much better characterisation especially of the nucleation stage.

Therefore, the aim of this work is to prepare gold nanoparticles stabilised by ionic liquids and study the processes of nucleation and growth of the nanoparticles in real time, using various techniques for chemical and structural analysis such as X-ray absorption and UV-Vis spectroscopies, as well as small angle X-ray scattering (SAXS) and high resolution transmission electron microscopy (HRTEM).

Preliminary results obtained with UV-Vis and XAFS spectroscopies as well as SAXS will be presented. UVvis enabled to follow the evolution of the characteristic gold plasmon band as a function of the synthesis conditions, while size and morphology have been characterised by SAXS. Speciation of gold in solution is under study using EXAFS.

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Digital soil mapping: broadening soil understanding across scales

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Soil is a natural resource that covers almost all continental regions and can be considered the skin of Planet Earth. Soil regulates climate, cycles nutrients and serves as a substrate for plants growth which, in turn, are source of food and fiber. Soil is the interface between the atmosphere, hydrosphere and biosphere. The importance of this natural resource was recognized by the United Nations (UN) with the declaration of 2015 as the International Year of Soils. There is an increasing demand for soil spatial information for its proper use and conservation. Scientists and decision makers, who are dealing with environmental sustainability and climate change, are adding up to agronomist, dealing with crop production, in the need of soil data. Unfortunately there is a lack of available soil inventories, and the ones ready to use are sparse and in very small scales. In recent years, Pedologiests have promoted a shift from qualitative towards more quantitative methods of soil mapping. The application of mathematical and statistical methods for study of the distribution and genesis of soils, named Pedometrics, has made possible the application of Digital Soil Mapping (DSM) [1], towards generating digital soil information linked to uncertainty. DSM is defined as “the creation and the population of a geographically referenced soil databases generated at a given resolution by using field and laboratory observation methods coupled with environmental data through quantitative relationships.” Researchers have proven that coupling DSM to novel methods of soil sampling, as Proximal Soil Sensing, is effective in producing soil spatial information readily available for decision making [2]. Nowadays, demand driven projects have produced, not only soil class maps, but also properties maps as carbon content, fertility and texture.

In this scenario, our research group has been studying and applying new possibilities of producing soil maps and inventories [3, 4, 5]. We are using remote and proximal sensing, legacy soil data, pedologists tacit knowledge and newly acquired samples for predictive modelling of soil types and properties. A main challenge of our studies is to increase the scale of the produced information towards higher detailed maps, in the same time that, uncertainty is known and identified in all modeling steps. Integration of technologies, for field and laboratory soil sampling, is another critical issue in the research area of soil mapping. At SyncLight 2015 School in Recent Developments in Synchrotron Radiation we aim into gaining knowledge, and stablishing partnerships, towards using LNLS facilities for soil mineralogical characterization, soil genesis and lithology. Estimation and characterization of soil organic matter is also an important application which we intend to apply synchrotron radiation. All these information will be applied in better understanding the effects of land use changes and dynamics in soil and its functions in the environment.

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Structure and function of Baeyer-Villiger Monooxygenases from *Aspergillus flavus*

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Bayer-Villiger monooxygenases (BVMOs) are flavin-dependent enzymes that catalyze the conversion of ketones and cyclic ketones to esters and lactones, respectively, by using molecular oxygen as oxidant and NAD(P)H as electron donor [1]. BVMOs have been studied primarily for their role in biocatalysis, as a more environmentally friendly alternative to chemical Baeyer-Villiger synthesis. BVMOs occur in bacteria and fungi, but not in higher eukaryotes such as plants and animals. Bacterial BVMOs have been widely studied, and the crystal structures of several bacterial BVMOs have been solved. However, fungal BVMOs have not been studied to the same extent. The filamentous fungus *Aspergillus flavus* is a notorious producer of aflatoxins, which are carcinogenic secondary metabolites that contaminate certain agricultural crops [2]. The genome of *A. flavus* contains a total of 26 putative BVMO genes, of which the function of only one is known – MoxY, a key enzyme in aflatoxin biosynthesis [3]. In this study, MoxY and 10 of the BVMO homologues from *A. flavus* were heterologously expressed in *E. coli,* and their biocatalytic abilities investigated, both as whole-cell biocatalysts and purified enzymes. MoxY and the BVMO homologues displayed divergent specificity with regards to substrate acceptance, profiles with regards toas well as regio- and enantioselectivity, and accepted a wide range of ketone substratesdespite their high sequence similarity and phylogenetic clustering [4].

The homologue BVMOAfla838 was crystallized in the presence of FAD and NADP and the structure determined at 2.1Å. The overall structure of BVMOAfl838 closely resembles bacterial BVMOs, and consists of a FAD-binding domain and an NADP-binding domain. Crystallization in the absence of NADP resulted in a number of regions with low no electron density, supporting that, similar to bacterial BVMOsS, BVMO¬Afl838 consist of several highly mobile regions that are stabilized in the presence of NADP(H) to facilitate catalysis.

BVMOAfl838 represents the first crystal structure of a fungal BVMO to be solved. Although the structure of MoxY remains elusive, crystal structures of closely-related homologues, such as BVMOAfl838, may allow homology modelling of MoxY. A 3D structure of MoxY can give a unique insight into aflatoxin biosynthesis from a structural perspective, and will provide a new angle to study the control of aflatoxin biosynthesis.

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Thermal annealing of photoanodes based on CdSe Qdots sensitized TiO_2 nanotubes

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Quantum dot sensitized solar cells (QDSSCs) are a type of third generation PV devices which aim towards conversion efficiencies beyond the Shockley-Queisser limit i.e. the thermodynamic limit of the light to electric power conversion efficiency of a single junction PV cell, through advanced concepts such as multiple carrier generation by impact ionization and multijunction tandem cells [1]. To build QDSSCs photoanodes, semiconductor quantum dots (Qdots) which act as optical sensitizers are deposited onto wide-bandgap semiconductor nanostructures.

In this work, we studied the thermal annealing effect on photoanodes consisting of TiO_2 nanotubes sensitized with CdSe Qdots by direct adsorption [2]. Qdots were synthesized by "Hot injection method" [3]. Heat treatment of photoanodes in air can cause either an improvement or a serious drop in the photocurrent generation. Ligands or capping agents stabilize Qdots removing highly reactive dangling bonds on its surface but also they can act as a passivating layer that increases charge transfer resistance between Qdots and TiO_2 nanotubes [4]; therefore optimal conditions of thermal annealing are needed to improve efficiency of interfacial charge transfer avoiding as far as possible the decomposition of the sensitizers. As a corollary of this study, a 2.5- fold increase in photocurrent value was reached after thermal annealing at 200°C during at least two hours; while thermal treatments at temperature values higher than 250°C can produce a deleterious effect on the conversion efficiency if the annealing time extends over a long period of time. Photoelectrochemical techniques were used as tools for mechanistic dilucidations of the observed behavior.

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Organic Electronics and Printed Devices

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One of the main researches developed by the Polymers Group 'Prof. Bernhard Gross' deals with organic electronics and printed devices for several applications such as photovoltaic cells (OPV)[1], field effect transistors (OFET), luminescent devices (OLED and electrochemical cells [OLEC][2]) and sensors of different kinds[3,4]. Most of them are made from soft materials, either synthesized organic molecules or extracted from biological sources, processed by wet methods. These research aspects pose some challenges when compared to silicon technology but also have their advantages. Performance is usually the bottleneck of organic devices technology mainly due to system disorder which hampers charge transport, but, in contrast, it is possible to process materials by several techniques of which the most interesting are the printing ones[5]. Moreover, most devices are made from nanometric thin films and so a fine tuning among active layer, substrate, solvent choice and another bunch of parameters is needed to achieve good films morphology and structure. For example, in OFET's it is desirable that the material be crystalline (or partially) and the pi stacking direction should be parallel to channel width. This morphology can be tuned by changing solvents, the substrate surface energy and even the molecule side chains. Printing techniques are the most promising for large-scale production of organic based devices since it cheapens the process. Ink-jet and roll-to-roll process are the most studied. Currently, we are developing roll-to-roll processing for LEC and OPV, and ink-jet for OFET and biosensors with some preliminary, but interesting results.

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Research on the magnetic behavior of multilayer and nanowire structures

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Magnetic control at the nano-scale is interesting for technological applications. Nowadays, several ways to obtain this control have been reported and the development of new materials to improve it is growing up. In our research group, we develop and study magnetic properties of nanowire and multilayer magnetic films. Our currently research focus on the study of magnetic behavior of ferromagnetic films coupled to another material with antiferromagnetic, superconductor or ferroelectric properties. Also, we work with ferromagnetic films which show first order phase transitions trough changes in temperature, as well as, ferromagnetic films coupled to materials which show temperature- or field-driven structural phase transition.

More specifically, we study the magnetic behavior of the NiTi/Co and NiTi/Ni films through the structural phase transition of the nearly equiatomic NiTi layer. The films have been grown on silicon (100) substrates by DC magnetron sputtering. In this structure, the magnetization of the ferromagnetic layer may be modified through changes in the stress field at the interface, when the structural phase transitions in the non-magnetic layer is carried-out. Other proyect in the group is the study of ferromagnetic/superconductor bilayers and superconductor spin valves. Experimentally, a strong interaction between both subsystems could drastically change the properties of the constituent materials. The interaction is due to the induced magnetic field from the no uniform magnetization in the ferromagnetic subsystem which goes through the superconductor producing a vortex structure. One option to obtain the no uniform magnetization is by using ferromagnetic nanowires or by the own topology given by the wall domains in a continuous film. In our group, nanowires of Ni and Co are produced by anodizing an aluminum sheet to grow up a porous oxide layer. Inside these pores the magnetic material is deposited by chemical electro deposition technique. Another research project is about spin valves such as multilayers thin films with different antiferromagnets of cubic anisotropy and Ni-Cu alloys films, which are sputter deposited on silicon (100) substrates. Finally, we research about the properties of magnetic solids which show first order phase transitions near room temperature. We are studying Heusler alloys such as Ni_2MnGa and Ni_2MnIn with the idea of development materials devices for magnetic cooling. Also, FeRh films will be sputter deposited on MgO substrates or ferroelectric substrates as $BaTiO_3$ with the porpouse to be used as new media of high density digital information storage.

All these functional structures are characterized by X-ray diffraction (XRD) and Rutherford backscattering spectrometry (RBS) to obtain the crystal structure and chemical composition respectively. Magnetic measurements as a function of temperature or magnetic field are performed by using a superconducting quantum interference device (SQUID) and a vibrating sample magnetometer (VSM) to study anisotropy behavior, coercivity, magnetic phase transitions, etc.

Use of raw powder glass residues as a new silica source for hydrothermal synthesis of MFI and MEL zeolites with hydrofluoric acid

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Raw powder glass is unable to be included in the usual broken glass recycling process [1]. Due to its proportion of SiO_2, it is a suitable T^{IV} source to produce zeolites [2]. So, the objective of this project is to obtain MFI and MEL zeolites, two of the most versatile zeolites used for catalysis and adsorption, by hydrothermal synthesis employing HF as mineralizing agent.

The zeolites were successfully obtained employing this silica source treated with a hydrochloric acid solution (in the MFI synthesis) and as provided. Synthesis were performed using hydrofluoric acid as mineralizing agent and tetrapropylammonium hydroxide (MFI) or tetrabutylammonium hydroxide (MEL) as organic structure-directing agent [3]. Scanning electron microscopy and x-ray diffraction were employed to characterize the products. In the MFI synthesis, x-ray diffraction patterns identified the resulting products as Fe-silicalite-1 and allowed calculating Si/Fe ratio in comparison with existent literature data [4]. Presence of iron was also confirmed by ν(Si-O-Fe) symmetric stretch in the infrared spectra [5].

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Microstructural analysis of severely deformed materials using X-Ray diffraction and EBSD

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Severe plastic deformation techniques improve the mechanical properties of a material by affecting its microstructure, decreasing domain sizes and accumulating defects, mostly dislocation arrays and stacking faults. The complexity of such microstructure requires the combination of different techniques for a complete analysis, including both local and global microstructural information. For the former analysis, Electron Back Scatter Diffraction (EBSD) allows not only to observe the microstructure at nanometric resolution but also to characterize local crystalline orientation and misorientation. This information can be correlated to the microstructural analysis carried out by global techniques, such as X-ray diffraction; through peak broadening and shape analysis, this technique allows to quantify the presence of different microstructural features affected by deformation, such as domain sizes, dislocation and stacking fault densities, and compactness of dislocation arrays [1][2]. This analysis can be performed on diffraction data obtained in various instruments with different wavelengths and angular dispersions, determining in this way the sensitivity of the technique to the energy and brilliance of the instruments. In particular, this analysis can be carried out in data obtained from different diffracting planes in the samples, allowing the study of the anisotropic microstructure determined by deformation through the construction of Generalized Pole Figures (GPFs) [3].

The analysis was performed on F138 stainless steel samples deformed by equal-channel angular pressing at room temperature and 300°C, in order to compare grain refinement and twin and dislocation boundary development. The microstructural anisotropy determined by cold rolling was also analyzed for Al, Cu and F138 steel samples, by the determination of GPFs. The diffraction patterns were obtained at an X'Pert PRO diffractometer and at LNLS and DESY synchrotron facilities.

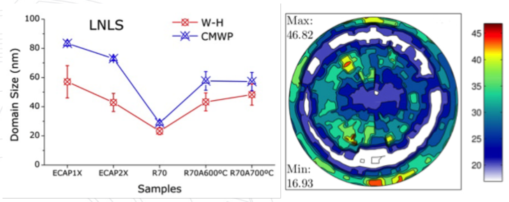

Fig. 1: (a) Domain size obtained for F138 samples deformed by ECAP and cold rolling and (b) domain size (111) pole figure obtained for a cold rolled sample

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In Situ X-Ray Diffraction Study on Liquid Crystal Materials

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X-Ray scattering provides us a very fundamental method for structure analysis of soft materials, such as liquid crystals. Liquid crystal is a special state of matter, between crystalline solid and isotropic liquids. The orientational and positional orders of liquid crystals enable them to self-assemble into interesting and exotic nanostructures. In situ X-Ray diffraction (XRD) can be effectively utilized to understand the various phases that liquid crystals form, such as the nematic and smectic phases. The layer spacing of the smectic phases is calculated as $d=2\pi/q$. By using bent-core liquid crystal materials, we can form helical nanofilaments. Synchrotron X-Ray diffraction, small-angle X-Ray scattering (SAXS) and wide-angle X-Ray scattering (WAXS) allow us to study these helical nanofilaments in the B4 phase. By exploring the phases and phase transitions of bent-core liquid crystal materials using X-Ray diffraction, I aim to develop self-assembled nanoheterostructures and exotic materials

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Beam tracking approach for x-ray phase contrast and dark-field imaging

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X-ray phase contrast imaging plays a central role in the analysis and characterization of materials in a wide range of applications, such as biology, medicine and material science. The availability of highly coherent synchrotron sources has driven the development of several direct and indirect x-ray imaging methods, with the aim of achieving enhanced image contrast, resolution and phase sensitivity.We recently developed a new, quantitative x-ray phase imaging method [1], which can be considered a development of our Edge Illumination (EI) technique [2]. The two approaches have in common the fact that the sample is illuminated by a laminar (or "sheet") beam. However, while in EI an edge is used to analyse the beam, in the new implementation we used a high resolution detector to track the changes in the beam induced by the sample. This allows extracting absorption, refraction and ultra-small angle scattering without requiring any displacement of optical elements. As for EI, the "beam tracking" approach can be parallelized by using a series of slits (i.e. an absorbing mask). This "parallel" implementation of the beam tracking method can be easily translated for use with a laboratory setup [3], offering a simple "single-shot" method for x-ray phase contrast and scattering imaging. At the same time, the reduction in acquisition time enabled by tracking multiple beams, instead of having to displace a mask in multiple positions, allows for a simple and fast implementation in computed tomography, for the 3D reconstruction of the complex refractive index and scattering distribution of a specimen [4]. In addition to the above, we also developed a method that combines the idea of using a small laminar beam with the phase retrieval techniques characteristic of coherent diffractive imaging, through a ptychographic approach [5]. This approach exploits the high coherence available at certain synchrotron facilities and, through a more complex and computationally demanding phase retrieval procedure, improves the achievable resolution, providing higher sensitivity to the high frequency part of the sample's complex transmission function. All these methods were experimentally validated at the I13 beam line (coherence branch) of the Diamond Light Source facility (Didcot, UK), while the translation to conventional sources was developed in our laboratory at UCL (London, UK).

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Structural changes in lipid model membranes induced by a fungal peptide.

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Ece1-III is the third of seven peptides that are associated to the eponymic ECE1 gene, a growth-specific gene of the polymorph fungus *Candida albicans*. ECE1 is exclusively found in the yeast's hyphal appearance in which it has the ability to cause infections in humans. The peptide of our interest is the first explaining toxic effects of fungi and shows a strong lytic effect on human cells. We propose that Ece1-III behaves similar to antimicrobial peptides that partition into biological membranes due to their characteristic amphipathic alpha-helical secondary structure. The association to the membrane may finally lead to its permeabilization by one of three different pore-forming mechanisms described: (i) the 'barrel-stave model', (ii) the 'toroidal-pore model', or (iii) the 'carpet model'. Our aim is to reveal the interactions of the peptide with phospholipid membranes either by assigning it to one of the models described so far or to evolve a new one. The understanding of the interaction mechanisms is of high importance with a view to preserving the integrity of human cell walls.

The poster shows the results of a variety of biophysical techniques that characterize the lipid–peptide interaction with strong emphasis on synchrotron based methods (X-ray reflectivity, grazing incidence small-angle X-ray scattering, oriented circular dichroism).

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Recent Developments in Synchrotron Radiation

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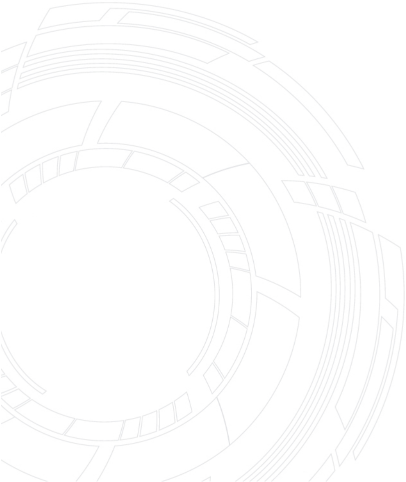

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