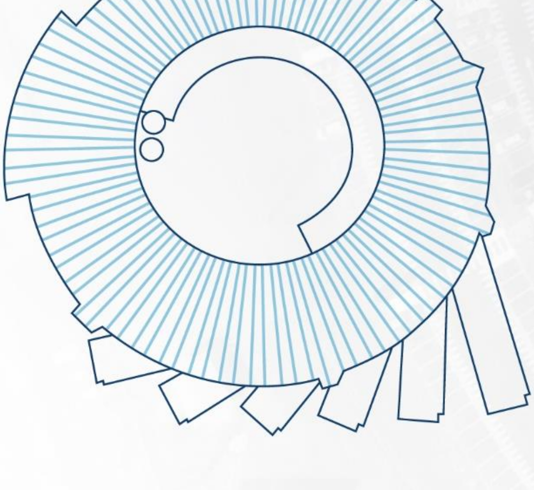
29th RAU
ANNUAL USERS MEETING LNLS/CNPEM

November 5-7th

2019



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FOREWORD

On behalf of the Scientific Committee, I warmly welcome all participants of the 29th Annual Users Meeting of the Brazilian Synchrotron Light Laboratory (29. RAU/LNLS).

After 22 years of continuous operation, with impressive numbers of users, proposals and publications the UVX-LNLS users' program has ended, with beam for users until August 1st for the completion of ongoing projects.

A cycle closes, but a brighter new cycle is just beginning: the Sirius source is coming. Important achievements from last year include: The start of the commissioning of the accelerators, with the first electron beam loop around Sirius' booster in March, and the first high-energy accumulation, 3 GeV, in October; The beginning of the assembly of beamlines and the installation of the optical elements in two of them, Manacá and Cateretê; Testing and commissioning with synchrotron light of several components, which will be installed in the beamlines, notably the four reflections x-ray monochromator (4 bounces crystal monochromator) and the Medipix-based ray detector, the PiMega detector.

In this exciting atmosphere we organized the 29th Annual Users Meeting. This year RAU includes, in addition to the scientific program with 90 poster presentations and 25 oral contributions, a record of six satellite events with ten invited speakers as well as the first LNLS Users Committee Assembly. The satellites will cover a variety of topics ranging from spectroscopy under in-situ and operando conditions, resonant inelastic X-ray scattering applied to free molecules and condensed matter, synchrotron-based techniques to characterize engineered nanomaterials in complex biological and environmental systems, micro and nano X-ray tomography, protein crystallography to mathematical and computational aspects related to data processing.

None of this would be possible without the dedicated work of the Local Committee and CNPEM staff, decisive for the organization of such a relevant meeting.

We are also indebted to the sponsors and main funding agencies Fapesp and CAPES, which helped to make this important event possible.

We wish you all a fruitful and vibrant event!

Maria Luiza Rocco

Chair of the 29th RAU

29th Annual Users' Meeting (RAU) PROGRAM

05/11 (Tuesday)

8:00-9:00	Reception and Registration
9:00-9:15	Opening: Welcome by the Scientific Committee
9:15-10:00	*Electronic and chemical properties of buried interfaces.* **Slavomir Nemsak**
10:00-10:45	*Computational imaging with synchrotron light.* **Doga Gursoy**
10:45-11:15	Coffee Break
11:15-12:45	3 satellites in parallel: Satellite 1 – CPU (Seminar room) Satellite 2 – NAPXPS (Plenary room) Satellite 3 – T-RHEXI (Mezzanine room)
12:45-14:00	Lunch
14:00-17:00	3 satellites in parallel: Satellite 1 – CPU (Seminar room) Satellite 2 – NAPXPS (Plenary room) Satellite 3 – T-RHEXI (Mezzanine room)
17:00-20:00	Panel sessions + Social gathering
20:00	Bus departure (Go Inn Hotel)

06/11 (Wednesday)

8:30-8:45	Opening by the Scientific Committee
8:45-9:15	Status of the Sirius project – **Antonio Jose Roque**
9:15-9:45	LNLS Science Highlights – **Yves Petroff**
9:45-10:15	Overview of Sirius Beamlines – **Harry Westfahl Junior**
10:15-10:45	Official Photo and Coffee Break
10:45-12:45	Communications sessions in parallel I
12:45-14:00	Lunch
14:00-16:00	Communications sessions in parallel II
16:00-16:30	Coffee Break
16:30-18:30	Plenary session with users and LNLS Users Committee Assembly
18:30-19:30	Sirius tours
19:40	Bus departure (Go Inn Hotel)

07/11 (Thursday)

8:30-9:15	*Nanomaterial-Biological System Interaction Studied by X-ray Imaging Techniques. (Web Conference)* **Chunying Chen**
9:15-10:00	*Local maps of potential energy surfaces and chemical pathways* **Alexander Föhlisch**
10:00-10:30	Coffee Break
10:30-12:30	3 satellites in parallel: Satellite 4 – TRIXS (Seminar room) Satellite 5 – NanoAHES (Plenary room) Satellite 6 – SMX (Mezzanine room)
12:30-13:45	Lunch
13:45-16:15	3 satellites in parallel: Satellite 4 – TRIXS (Seminar room) Satellite 5 – NanoAHES (Plenary room) Satellite 6 – SMX (Mezzanine room)
16:20-16:30	Final remarks
16:30-17:00	Bus departure (Go Inn Hotel, VCP/GRU Airports)

SATELLITE EVENTS PROGRAM 05/11

COMPUTATIONAL PROCESSING FOR USERS (CPU)

Time	Activity	Invited Speaker
11h20-11h30	Opening remarks	**Eduardo Miqueles (LNLS)**
11h30-12h00	The PIM3GA Detector: an overview	**Dawood Alnajjar (LNLS)**
12h00-12h40	Computational methods and challenges in high-throughput x-ray imaging.	**Doga Gursoy (APS)**
12h40-14h00	**Lunch**	
14h00-14h45	What is superiorization and how can it be Applied to tomographic image reconstruction.	**Elias Helou (USP)**
14h45-15h15	Strategies for image reconstruction at Sirius.	**Patricio Guerrero (LNLS)**
15h15-15h45	HPC, Storage, Data Access and User's dynamics for Sirius	**Fernando Furusato (LNLS)**
15h45-16h25	Automatic segmentation in large-scale 3D+T microscopy image data.	**Johannes Stegmaier (RWTH Aachen)**
16h30-17h00	High-Throughput and Integrated 3D/4D Image Visualization and Segmentation for Sirius	**Thiago Spina (LNLS)**

WORKSHOP ON NAP-XPS SCIENTIFIC CASES FOR SIRIUS (NAP-XPS)

Time	Activity	Invited Speaker
11:15-11:45	Colibri Beamline: NAP-XPS endstation	**Daniela Coelho/Flávio Vicentin**
11:45-12:45	Photoemission spectroscopy and microscopy studying solid/liquid interfaces	**Slavomir Nemsak (ALS)**
12h45-14:00	Lunch	
14:00-14:40	Probing the Nature of the Strong Metal-Support Interaction (SMSI) Effect by NAP-XPS measurements for Enhanced Catalysis	**Fabiano Bernardi**
14:40-15:20	Atomic Quantum Clusters: a Novel Material at the Bottom of the Nanoscale. Stability of supported Cu5 in presence of oxygen.	**Felix Requejo (INIFTA)**
15:30-16:30	Near Ambient Pressure XPS (NAP-XPS) at the ALBA Synchrotron Light Source.	**Carlos Escudero (CELLS)**
16:30-17:00	Closing remarks.	**Daniela Coelho/Félix Requejo/Flávio Vicentin**

TIME-RESOLVED HIGH ENERGY X-RAY IMAGING MEETING (T-RHEXI)

Time	**Activity**	**Invited Speaker**
11h15-11h30	Opening Remarks	**Nathaly Archilha (LNLS)**
11h30-12h30	Benefits and Challenges of High Energy X-ray Imaging: Experience from Beamline I12, Diamond Light Source	**Thomas Connolley (Diamond)**
12h45-14h00	**Lunch**	
14h00-14h45	Mogno Beamline – a scientific overview	**Nathaly Archilha (LNLS)**
14h45-15h30	4D study of groundwater remediation using nano and chemical based technologies	**Tannaz Pak (Teesside University)**
15h30-16h15	In vivo X-ray Imaging using synchrotron radiation	**Murilo Carvalho (LNLS/LNBio)**
16h15-16h45	Mogno Beamline – an engineering overview	**Gabriel Schubert (LNLS)**
16h45-17h00	Closing Remarks	**Regina Cély Barroso (UERJ)**

SATELLITE EVENTS PROGRAM 07/11

TRENDS ON RESONANT INELASTIC X-RAY SCATTERING (TRIXS)

Time	**Activity**	**Invited Speaker**
10:30 -10:40	Openning	**Luiza Rocco e Tulio Rocha**
10:40 – 11:40	Resonant inelastic x-ray scattering of correlated electron systems.	**Marco Moretti**
11:40 – 12:00	Vibrational, electronic, and magnetic excitations by laser Raman spectroscopy: case studies for future RIXS experiments.	**Eduardo Granado**
12:00 – 12:20	Potential applications of RIXS to study dynamics of charge carriers, recombination centres and defect levels in luminescent materials.	**Mario Valério**
12:20 – 13:45	**Lunch**	
13:45 – 14:50	RIXS on Molecular Systems	**Alexander Föhlisch**
14:50 – 15:10	Electron spectroscopy on micro-jets inspiring breakthrough experiment on RIXS	**Arnaldo Brito**
15:10 – 15:30	Femtosecond Electron Transfer Dynamics of Semiconductors Probed by the Core-Hole Clock Spectroscopy.	**Soheila Holakoei**
15:30 – 16:00	RIXS at IPE beamline	**Thiago Mori**
16:00 – 16:15	Final remarks	**Tulio Rocha**

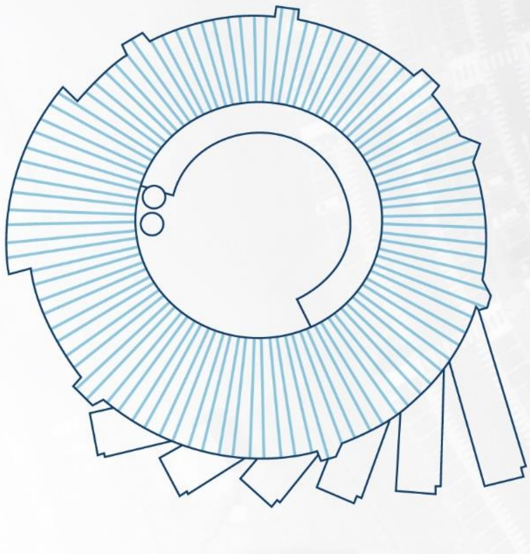
NANOMATERIALS APPLIED TO HEALTH AND ENVIRONMENTAL SCIENCES (NANOAHES)

Time	Activity	Invited Speaker
10:30 – 10:45	Workshop opening	Carlos A. Pérez and Hudson W. Carvalho
10:45 – 11:30	Sub-micron X-ray microspectroscopy for life and environmental nanotoxicology.	**Hiram Castillo-Michel (ESRF/France)**
11:30 – 12:00	Hyperspectral chemical imaging in space and time using synchrotron light.	**Dario Ferreira Sánchez (PSI/Switzerland)**
12:00 – 12:30	Nanomaterials in agriculture and enviroment: moving towards realistic experimental conditions.	**Hudson W. Pereira de Carvalho (CENA/USP-Brazil)**
12:30 – 13:45	**Lunch**	
14:00 – 14:45	Characterization of the pharamcokinetics and metabolites of metal-based nanomaterials in biological system.	**Chunying Chen (CAS/NCNT- China)**
14:45 – 15:15	Nanoparticles-cell interaction probed by x-ray microscopy.	**Mateus Borba Cardoso (LNNano/CNPEM-Brazil)**
15:15 – 15:45	Scientific opportunities at Sirius in health and environmental toxicology.	**Carlos Alberto Pérez (LNLS/CNPEM-Brazil)**
15:45 – 16:15	Open discussion and closing remarks	
16:20 – 16:30	LNLS User´s meeting closing remarks	

MX AT SIRIUS AND EMERGING TOOLS FOR DRUGS DISCOVERY

Time	Activity	Invited Speaker
10:45 – 11:00	The MANACA beamline at Sirius, status report on strategies to be available to users.	**Ana Carolina Zeri (CNPEM)**
11:10 – 12:30	MXCuBE3 – the future of the MXCuBE collaboration.	**Daniele de Sanctis (ESRF)**
13:45-14:15	Status of the implementation of MXCuBE3 for the control of the Manaca beamline.	**Lais Pessine do Carmo (CNPEM)**
14:15- 15:00	Sample Holders for serial crystallography at the Manaca beamline.	**Evandro Araujo (CNPEM)**
15:00 – 16:10	Visit to the Manaca beamline and chat with the beamline staff and Daniele de Sanctis	

ABSTRACTS



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Invited Plenary Lecture 2

COMPUTATIONAL IMAGING WITH SYNCHROTRON LIGHT

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Recent years witnessed a proliferation of hard x-ray imaging instruments at synchrotron and laboratory-based facilities that can provide spatial resolution down to few tens of nanometers. Imaging of specimens at these fine scales is particularly challenging, because of the reduced photon efficiency, higher radiation doses, and inaccuracies of the stages that lead to noisy and sparse datasets. Besides, these microscopy techniques pose a new level of challenge for imaging applications in terms of data rates, volumes and complexity. In this talk, I will present a review of the current status of techniques and computational x-ray imaging approaches to alleviate these issues in practice. I will also talk about the scalable implementation of these algorithms and their applications at high-throughput imaging beamlines of the Advanced Photon Source.

Invited Plenary Lecture 3

NANOMATERIAL-BIOLOGICAL SYSTEM INTERACTION STUDIED BY X-RAY IMAGING TECHNIQUES

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Many nanomaterials are useful in biological detection, diagnosis, and therapy for diseases and have shown great potential for biomedical applications. Therefore, the toxicity of nanomaterials becomes an increasing concern. Both in vitro and in vivo studies were applied to evaluate biological consequence of nanomaterials. We summarize our recent progress of probing the nano-bio interaction of nanomedicine, focus on the driving force and redox reaction at nano-bio interface, which have been recognized as the main factors that regulate the functions and toxicities of nanomedicine.

The intrinsic physicochemical properties of nanomaterials have decisive influence on their biological consequences and toxicity. These properties include size, shape, surface charge, chemical composition, surface modification, metal impurities, agglomeration and dispersion, degradation, as well as the formation of “protein corona”. It is important to obtain a better understanding of the uptake, trafficking, pharmacokinetics, clearance, and role of nanomaterials in biological systems, so that their possible undesirable effects can be avoided.

Development of adequate and specific analytical protocols or methodologies for the quantification of NMs/NPs in nanosafety, nanomedicine and biomedical nanotechnology studies have been proposed. Synchrotron radiation, which is highly polarized, tunable, and concentrated over a small area, plays an indispensable role for nanotoxicology studies. As an example, in our study, the combination of ICP-MS, synchrotron-based scanning transmission X-ray microscopy (STXM), microbeam X-ray absorbance near edge structure (μ-XANES) and μ-SR-XRF have simultaneously provided information about the subcellular distribution and chemical species of metal-containing nanomaterials of interest

POSTER PRESENTATION

A STUDY ON THE LIMIT OF APPLICATION OF THE KINEMATICAL THEORY OF X-RAY DIFFRACTION

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The key to practically all the properties of matter is in the crystal structure, to know how the atoms are distributed in space is a fundamental information for modern science. X-ray diffraction is among the most suited techniques to obtain this atomic structure from measured angular position and intensities of the diffraction peaks. In order to describe the process of X-ray diffraction, it was initially used the kinematical theory, also known as geometric theory, because basically uses geometric factors, such as Bragg's law, for the description of the phenomenon. Over time, some experiments showed a disagree with the geometric theory, for example the experiment realized by G. Borrmann, that observed an anomalous transmission effect on the X-ray beam when passing through a crystal of great thickness. Another theory was developed, the so-called dynamical theory of X-ray diffraction, which takes into account several physical principles, such as the multiple scattering and index of refraction inside the crystal, and dynamical theory has been able to explain the Borrmann effect. With the advancement of science, new applications using dynamical theory began to be developed, such as X-ray diffraction imaging, where the observed contrast in the images originated from the difference between kinetical and dynamical intensities, x-ray standing wave (XSW), where the multiple reflections inside the crystal, give rise to a standing wave, which together with a fluorescence detector, provide a tool capable of elementary mapping the unit cell. Moreover, in X-ray optics where single crystals with a high degree of perfection are used as monochromators, dynamical theory is used to explain exactly the properties of the beam, such as energy. For this study we simulate measurements of X-ray diffraction using both the diffraction theories and we observe in what size of crystallite, the diffraction theories begin to diverge. The result shows that if the crystal has a thickness of 20% of extinction length, the intensities calculated by the kinematical and dynamical theories have a difference of 10%. Taking into account the absorption of the crystal, this size is still smaller.

KEYWORDS: X-RAY DIFFRACTION, KINEMATICAL THEORY, DYNAMICAL THEORY, LIMIT OF APPLICATION

POSTER PRESENTATION

AL AND ZR PILLARED CLAYS: A STUDY OF THE STRUCTURE BASED ON THERMAL CHANGE USING XRD AND XANES

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Pillared clays (PILCs) are obtained by intercalating polycations of different species and thermal treatment [1]. They have multiple technological applications due to their high specific surface and tailorable pore size; characteristics attributable to the natural nanostructure of the parental clay. In the natural clay, these characteristics are lost with thermal treatment, while conserved in the pillared clay due to its higher thermal stability. Furthermore, calcination is necessary because the intercalated clay is metastable, as the interleaved polycations themselves. Thermal treatment transforms the polycations into stable oxi-hydroxide phases named pillars. X-ray absorption near-edge structure (XANES) has demostrated to be a suitable for clay minerals and clay-based materials characterizations [2]. Different Species have been reported as been used as precursors of said pillars, being the most studied the Al13-Keggin polycation. Another interesting option for the pillaring are Zr precursors, as ZrO_2 is a promising pillar-material due to its high thermal stability and high acidity. This work looks to describe the structure of two pillared clays: an Al13 and a Zr-pillared bentonite at different firing conditions, comparing those results with the original clay. Particular focus was made in the analysis of the local structure of Al and Si. Both pillared clays were prepared using an Argentinian unpurified bentonite. Pillaring reagents used for the pillared clays were a) a polymeric hydroxyl-Al solution and b) a partially hidrolized $ZrOCl_2$ solution. In order to characterize the material, X-ray diffraction (XRD), scanning electron microscopy (SEM) and simultaneous thermogravimetric and differential thermal analysis (DTA-TG) of the materials were complemented with XANES. The d001 of the montmorillonite structure collapsed at 400°C, while the Zr-pillared clay maintained this (shifted) value up to 600 °C and the Al-pillared clay up to 800°C. Further thermal treatment produced the loss of the characteristic clay structure, and only a glassy phase with a low amount of quartz and feldspar was observed by XRD in all samples. Thermal treatment caused greater mass loss in the pillared clay due to the presence of the Zr-OH and Al-OH oligomers allocated in the interlayer space of the montmorillonite, being the mass loss higher in the Al pillared clay due to the higher amount of OH^- and H_2O in the structural formula pillaring precursor. The Al K XANES spectra confirmed the octahedral aluminum coordination in native montmorillonite, being this coordination progressively lost with thermal treatments at increasing temperatures, giving place to the presence of a four folded coordination. In the intermediate treatments, it presented some three and five coordination slight contributions. Also, the Si K XANES spectra do not change with temperature, indicating the stability of Si environments. The results confirm the potential of synchrotron-based techniques for characterization of natural materials and its derived composites, in particular ones with low crystallinity. In particular, Zr-pillared montmorillonites aluminums Si and Al K-XANES spectra have not been reported before.

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KEYWORDS: BENTONITE, PILLARED CLAYS, XANES

POSTER PRESENTATION

AMYLOIDOGENIC MODEL PEPTIDES AS CATALYSTS FOR STEREOSELECTIVE ALDOL REACTIONS

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In this work, the self-assembly in an aqueous medium of two compounds derived from amyloid-like structures, [RF]4 and P[RF]4 (where: R = arginine; F = phenylalanine; P = proline), was studied by using spectroscopy, microscopy, and scattering techniques. The peptides presented a similar critical aggregation concentration (cac) considering the same medium conditions (~0.35 mmol L^{-1} at 25°C). The stability of the systems was analyzed by zeta potential measurements, which showed that under acidic and neutral conditions the colloidal particles remained stable, and for basic solutions, strongly interacting colloids and supramolecular aggregates in solution were observed. CD data confirmed the changes in the conformation of the secondary structures for both compounds by changing the pH of the solution. By SAXS, the curves were fitted using a fractal structure factor, and we observed that the size of the monomers that compose the fractal aggregates of [RF]4 is twice as large as that of P[RF]4. These compounds showed potential as catalysts in aldol reactions, using cyclohexanone and p-nitrobenzaldehyde. In this case, under optimized reaction conditions, 78% conversion (ee up to 85%) was observed in [RF]4 solutions, while P[RF]4 had only 51% conversion (ee up to 85%). Our results show, for the first time, a dependence of the morphology on the stereoselective aldol reactions, whereas the folding arrangement of the chiral assemblies in the polypeptide chains plays an essential role in the access of the reactants to the active surface sites.

KEYWORDS: AMYLOIDOGENIC PEPTIDES, ALDOL REACTIONS, CATALYSIS, SUPRAMOLECULAR CHEMISTRY, STEREOSELECTIVE REACTIONS, SAXS

ORAL PRESENTATION

ANALYZING IN-SITU CRYSTALLIZATION OF BISMUTH FERRITE THROUGH X-RAY DATA ANALYSIS

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Advanced synchrotron sources of high flux and detector systems capable of collecting, in just a few seconds, full X-ray diffraction (XRD) patterns of powder samples create opportunities for IN-SITU studies of a variety of processes such as catalysis, energy storage and conversion, and crystallization of nanoparticles from amorphous precursors. There will be thousands of XRD patterns containing information on strutural changes along the processes [1]. Particulary in the case of crystallization, information on particle size, crystal phase, and lattice strain as a function of time and temperature, covering the whole process from amorphous to fully crystalline phases. Diffraction peak widths, peak positions, and integrated intensities (peak area above the background) have to be extracted as soon as the crystalline phases begin to form. Massive data analysis of XRD patterns is one current trend in crystallography mainly due to diffraction peak overlaping, changing of peak line profiles and shifting of peak positions during the processes, as well as irregular background intensities. In this work, we developed methods for studying IN-SITU crystallization processes, which are applied in the case of bismuth ferrite ($BiFeO_3$), or simply BFO. BFO is a magnetic and strong ferroelectric material at room temperature [2]. It is an important single-phase multiferroic material with potential for innovative technological applications in electromagnetic devices, optoelectronics, and spintronics. Wet chemical methods for synthesizing nanoparticles of BFO are attractive due to simplicity and possibility of controlling particle size [3]. In this sense, a detailed understanding of the crystallization process of BFO from amorphous precursors is important for improving chemical routes of synthesis and control of advanced production methods for this material. Data collection were carried out at XRD1 beamline of the Brazilian Synchrotron Laboratory (LNLS) using monochromatic x-rays of 12 keV (exact wavelength of 1.033012 Å). The precursor material is placed inside a quartz capillary and heated by hot air, while full XRD patterns are collected on time intervals of 38 s during hours. Our data analysis of two crystallizations of the same precursor material under different conditions lead to a simple equation for predicting grain sizes as a function of time and temperature. It also provides evidence of very high thermal expansion coefficients acting on nanoscales, at the beginning of crystallization when crystal grains are below than 30\,nm in size. This can be a new phenomenon to be further investigated in the near future with improved instrumentation (high x-ray flux and shorter counting times).

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KEYWORDS: CRYSTALLIZATION, IN-SITU, BISMUTH FERRITE

POSTER PRESENTATION

ANALYZING THE STRUCTURE FACTOR OF NANOPARTICLES INTERNALIZED BY CARCINOMA CELLS

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Magnetic nanoparticles (MNP) are widely used in biomedical applications such as drug delivery, MRI and magnetic hyperthermia [1]. Due to the magnetic characteristics, MNP tend to aggregate, this problem is solved coating the MNP with an organic surfactant shell [2], but, when MNP are internalized by living cells, these are enclosed in highly concentrated structures called endosomes, where the inter-particle distance is reduced increasing the magnetic interaction. For this reason, MNP properties related with the magnetic interactions are modified [3] and how particles are structured inside endosomes must be studied. In this work, MNP different in size, morphology and chemical composition were internalized by B16-f0 murine melanoma cells cultured in vitro. MNP in colloidal suspensions and internalized cells cultures were analyzed with SAXS technique. SAXS patterns were fitted using a spherical form factor (F(r,q)) model and a LogNormal size distribution (g(r)), the structure factor (S(q)) were added following the monodisperse approximation model. From SAXS patterns, MNP morphological parameters and the experimental S(q) were retrieved and compared with the fitted structure factor. Results show that the correlation peak positions is different for colloidal and internalized samples. Due to particle magnetic moment controls the structuring of MNP, for samples with smaller particles a mass-fractal structure factor describes the experimental S(q) while a sticky hard sphere structure factor describes the structuring of samples with bigger particles. The bigger the particle the more compacted structure.

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KEYWORDS: SAXS, STRUCTURE FACTOR, NANOPARTICLES

POSTER PRESENTATION

APPLICATION OF NI/SRTIO$_3$ NANOPARTICLES IN THE PHOTODEGRADATION OF METHYLENE BLUE

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Methylene blue is a widely used dye that gives serious environmental issues, especially concerning the water's quality. There are methods to transfer dyes from solid to liquid phase but side pollution is produced [1]. An efficient method to degradate this dye should be studied. An interesting idea is to use the Sun's energy that arrives at Earth's surface with a power density of 200 W/m^2 [2] to induce the photodegradation of methylene blue by using catalysts [1]. Brazil has a great potential for the capture of this energy. However, due to the typical band gap of these catalysts only photons of the ultraviolet region can be absorbed, which represents only 5% of the intensity of the solar spectrum at the Earth surface. Ni/SrTiO$_3$ nanoparticles are able to extend the absorption of the ultraviolet radiation to the visible region of the spectrum [3], then increasing the photocatalytic activity. In this work, Ni nanoparticles were synthetized according to previous work [4] and exposed to thermal treatments at 100°C, 300°C and 500°C during 1h in atmosphere aiming to tune the Ni size and oxidation state. After, these Ni nanoparticles were supported on commercial SrTiO$_3$ and applied to the methylene blue photodegradation using a homemade photoreactor, which is equipped with two 15 W lamps that simulate the solar spectrum. After the reaction, UV-Vis measurements showed a photocatalytic activity increase of up to 20% in comparison to the nanoparticles without thermal treatment. The nanoparticles were characterized by X-ray diffraction (XRD), small angle X-ray scattering (SAXS), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) techniques before and after the reaction. The XRD patterns showed the presence of the SrTiO$_3$, SrCO$_3$ and TiO$_2$ crystalline phases for the support and Ni and NiO for the nanoparticles. Rietveld refinement results showed a mean size of the SrTiO$_3$ and Ni nanoparticles of 35 nm and 2 nm, respectively. SAXS curve fitting suggests SrTiO$_3$ nanoparticles with mean size in accordance to the XRD results and show that Ni nanoparticles present two distinct nanoparticles population: a spherical one and a core-shell like structure formed by the Ni and oxidized Ni phases. The TEM images indicated an agglomeration of the nanoparticles with the thermal treatment employed. The XPS measurements allowed to identify the oxidation state of the nanoparticles, which are correlated with the photocatalytic activity results.

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KEYWORDS: CATALYSIS, SAXS, XPS, XRD, TEM, NANOPARTICLES

POSTER PRESENTATION

ARSENIC IN SOLUBLE MINERAL PHASES: μ-XRF AND μ-XANES STUDIES IN SALINE EFFLORESCENCES ASSOCIATED WITH MINE WASTES

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When sulfide-rich mine wastes are exposed to air and water, a series of reactions are triggered that produce acid mine drainage (AMD) and the development of newly-formed secondary mineral phases. The AMD generation is a serious environmental concern over the Puna region of Argentina, where a number of abandoned mines such as the Concordia Mine are found. Arsenic is one of the most hazardous contaminants associated with AMD due to its toxicity and high mobility in natural environments. However, it can also be scavenged by secondary minerals by either co-precipitation or adsorption [1, 2, 3]. Therefore, the aim of this work is to analyse the As solid speciation in saline efflorescences precipitated in the mining site. The samples were collected from the surface of the tailings dams and the streambed of Concordia stream, and were classified according with their colour (yellow, red and blue salts). Mineralogy was characterized by XRD and SEM/EDS. μ-XRF and μ-XANES measurements of salts and reference compounds (scorodite, As(V)-jarosite, As(V) schwertmannita and Na-arsenate) were performed at the XRF beamline in the Brazilian Synchrotron Light Laboratory (LNLS). The Kα X-ray fluorescence intensities of K, Ca, Fe, S and As were recorded so that a two-dimensional distribution could be mapped for each sample. The data were analysed using the PyMca software. Arsenic K-edge spectra (11,867 eV) were collected from 11,740 to 12,700 eV, at room temperature. The X-ray absorption near edge structure (XANES) spectra were analysed using the Athena program. The samples mainly consist of jarosite, and a mixture of schwertmannite and hydrated Fe sulphates. The μ-XRF mapping shows a generally homogeneous As distribution in the samples but higher concentrations are more frequently observed at the surface of Fe-rich mineral grains. this is also evidenced by positive and significant correlations between As and Fe. μ-XANES spectra of all the studied samples show edge features corresponding to As(V) compounds with E0 11,873.4. The results of the linear combination fits (LCF) indicate that As(V)-O compounds likely correspond to amorphous Fe arsenates adsorbed and/or co-precipitated onto jarosite and schwertmannite. These assignments coincide with previous XAS results and dissolution tests described in Nieva *et al.* [3] for the study samples. Because As is mostly associated with water-soluble phases, these efflorescences represent a hazardous source of contamination to the water reservoirs in the mine waste site.

KEYWORDS: μ-XANES, μ-XRF, DAM, ARSENIC

Oral Presentation

AUSTENITE REVERSION KINETICS AND STABILITY DURING TEMPERING OF AN ADDITIVELY MANUFACTURED MARAGING 300 STEEL

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Maraging steels are highly alloyed steels with a low carbon content which exhibit excellent mechanical resistance, combined with good toughness and ductility [1,2] which has been used largely in laser-based AM since its low carbon content helps to prevent thermal cracking upon cooling [3,4]. Martensite-to-austenite reversion has grown interesting as a manner to improve ductility, toughness and strain hardening, yet maintaining very high yield and tensile strengths [5,6] by triggering the TRIP (transformed-induced plasticity) effect. Many studies have found improvement of impact toughness and ductility by increasing the amount of reverted austenite in the microstructure in modified high Mn maraging steels [7,8]. Ex-situ studies can be time consuming under a trial-and-error approach. In-situ measurements using correlative synchrotron X-ray diffraction and dilatometry can be a more useful approach since the transformation kinetics can be time-resolved [9]. Isothermal heat treatments near the beginning of martensite-to-austenite transformation temperature (Ac1) are more effective to produce reverted austenite with high thermal stability when compared to isothermal cycles near temperature of complete austenitization (Ac3) [8,10]. Diffusion of austenite-stabilizing elements towards martensite lath/lath interfaces and previous austenite grain boundaries is the main mechanism for martensite-to-austenite reversion and stabilization in a compositionally homogenized martensitic matrix, may occurring at preexisting regions with high concentrations of austenite-stabilizing elements in non-homogenized matrixes [9], which can be relevant for additive manufacturing metallurgy. The work presents thermodynamic calculations, EBSD and in-situ synchrotron X-ray diffraction analyses to optimize, track and quantify phases content. Results showed that reversion between 610 and 690°C promoted microstructural refinement and a loss of capacity to stabilize reverted austenite at room temperature when the tempering temperature exceeds the critical threshold for efficient partitioning.

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Keywords: Maraging 300, Martensite-to-austenite reversion, Additive manufacturing

ORAL PRESENTATION

BAGASSE STRUCTURE MODIFICATIONS INDUCED BY PRETREATMENT ARE REVEALED BY COHERENT DIFFRACTIVE IMAGING

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In recent decades, the interest in the search for alternative energy sources has stimulated the use of plant bagasse generated as a product from ethanol production, such as the sugarcane waste in Brazil [1]. This material can be used as source of different sugars, for example, the cellulose, which can also be employed as a raw material in energy, paper and food industrial sectors. To extract cellulose, the bagasse must be submitted to chemical or physical processing such as the hydrothermal pretreatment [2]. The exploitation efficiency of the sugar extraction might depend on nanometric structural changes caused by the pretreatment [3]. Thus, we performed three-dimensional coherent X-ray diffractive imaging (3D CXDI) measurements of dry raw sugarcane (in natura) and hydrothermally pretreated bagasse samples, at ID10 beamline at ESRF (France), to verify changes in the porous network. In this presentation, we will propose a new methodology to prepare ~5 µm fragments of sugarcane bagasse and how the final ~30 nm spatial resolution three-dimensional allowed to perform accurate image analysis (segmentation). The CXDI experiments were a direct method to depict the morphological disruption of the fibrillar character from cellulose and the modifications in bagasse porosity. The understanding of porous network modifications is crucial to verify the material access to hydrolytic enzymes used in the further steps and is compulsory to determine and evaluate the pretreatment efficiency. Bagasse deconstruction is thematic which can be exploited by X-ray based techniques which will be soon feasible at Sirius.

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KEYWORDS: CDI, BIOMASS DECONSTRUCTION

POSTER PRESENTATION

BEHAVIOR OF HYDROTALCITE TYPE MATERIALS AS PRECURSORS OF CATALYSTS FOR REACTIONS OF ENVIRONMENTAL POLLUTANTS REDUCTION

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Hydrotalcites are minerals having hydroxide layers of Mg and Al in octahedral coordination with oxygen. The charge of each layer is compensated with carbonate. Synthetically, hydrotalcite type materials can be obtained using other divalent and trivalent elements and anions, in order to replace Mg, Al and the carbonate anion, respectively [1]. This flexibility allows the synthesis of new hydrotalcite type materials designed with particular compositional properties. This characteristic is appropriate to be exploited in Catalysis, from the standpoint of the synthesis of new catalysts obtained from oxides prepared by their calcination and catalytic behavior of as-synthesized and calcined materials in reactions of interest. We prepared a series of hydrotalcite type materials (precursors), tailored to specific applications leading to the abatement of environmental pollution, such as reduction of NO by CO with the aim of converting these two pollutants coming from automobile exhaust gases into N_2 and CO_2 [2]. The precursors for catalysts in the system Cu-Ni-Al-TA (TA being the terephthalate anion) were prepared by the co-precipitation method. The x ratio (Al/(Al+Ni+Cu)) was defined as 0.5 and y ratio (Cu/(Ni+Cu)) was varied. The catalysts was obtained by calcination of the precursor at 600°C (or 900°C) for 4 h with a heating rate of 10°C min^{-1} in static conditions (air atmosphere). This catalysts were characterized by XRD (at room temperature) using conventional diffractometer and by Synchrotron in the XPD beamline of LNLS. The results showed that layered compounds were formed at y values smaller than or equal to 0.7 and the catalysts possess the CuO, NiO, $CuAl_2O_4$ and $NiAl_2O_4$ phases. By Rietveld refinement was possible to quantify the crystalline phases in the catalysts. The X-ray absorption spectroscopy (XANES) gave information about the oxidation state of the catalysts at room temperature and under reaction conditions. This analysis showed that the Cu-catalysts obtained from the calcination of the precursor at 600°C have only Cu^{2+} species, and Cu^{+} and Cu^{0} species were found throughout the reaction of NO reduction by CO. However, even during pre-treatment at 500°C under helium flow, copper reduced species were also observed. According to TPR (Temperature Program Reduction) results, the introduction of a second metal decreased the reduction temperature of the monometallic catalysts. An easier reduction of copper oxide over nickel is also clear. Cu content, calcination temperature, compensation anion of the hydrotalcite and a pre-reduction of the catalysts significantly impact on the activity and selectivity of the catalysts. The performance of the catalyst with y = 0.5 showed similar performance of conventional Rh/CZ catalyst (CZ: CeO_2-ZrO_2) but with the advantage of presenting a much lower N2O yield.

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KEYWORDS: HYDROTALCITES, XRD, IN-SITU XANES, NO BY CO REDUCTION

POSTER PRESENTATION

BIOTURBATION DRIVES METAL BIOSSORTION BY BACTERIAL CONSORTIUM IN SURFACE SEDIMENT

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The processes and detailed interactions by which infauna bioturbation affect bacterial community are still poorly understood, especially under metal contamination. We evaluated depth distribution of bacterial electron transfer system activity, biopolymers (carbohydrate, protein and lipids) and metal concentration in contaminated muddy sediment (Cu(II), Zn(II) and Cd(II)) in microcosms at laboratory assays. Bacterial activity was high even under metal stress and positively related with the depths of bioturbation activity. The bioturbation activity was evaluated by quantifying geometric properties of the infauna galleries (volume, surface and perimeter) through microcomputed tomography. Further, ETSA was positively related with the amount of gallery surface and gallery perimeter, indicating the role of mucus on bacterial colonization and metabolic activity. Corroborating these finds, carbohydrate content was negatively related with ETSA and this relation depends on bioirrigation (indicated by gallery volume), suggesting that the increase in bioirrigation increases the rate of carbohydrate consumption by bacterial consortium, elevating the bacterial metabolic activity, even under metal stress. SR-µXRF maps of metal retention by bacterial biofilm and bacterial ETSA activity under metal stress through several carbon sources suggest that mucopolysaccharide production by burrow dwelling infauna enhances bacterial biofilm formation and metal immobilization at bioturbated zone, affecting positively the bacterial metabolism. Phylogenetic analyses suggest that bioturbation activity affect bacterial community structure in contaminated and bioturbated sediment by introducing metals from overlying water and introducing fresh organic matter through mucopolysaccharide production, favoring bacterial consortium that is able to colonize the negatively charged mucopolysaccharide, use the mucus as a carbon source and be resistant to metal contamination through biofilm formation.

KEYWORDS: BIOTURBATION, BACTERIAL BIOFILM, BIOSSORPTION, XRF

ORAL PRESENTATION

BOOSTING THE PHOTOCATALYTIC H2 PRODUCTION IN CERIUM OXIDE NANOPARTICLES

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The world is preparing to face a major energy crisis in the next decades [1]. Since the world population is growing and the fossil fuels inevitably is running out, new renewable and sustainable energy sources must be developed in order to supply the world's energy consumption in the near future. Moreover, the use of the fossil fuels and other energy sources that liberate CO_2 to the atmosphere contributes to the magnification of the greenhouse effect and, therefore, to the global warming [2]. In order to maintain the earth as a place where society can live in the future, replacement of the energy sources as fossil fuels for renewable and sustainable energy sources is mandatory and needs to be done immediately. Cerium oxide (CeO_{2-x}, $0 < x < 0.5$) presents optimum positions of the conduction and valence bands for photocatalytic H_2 production application. In the present work, cerium oxide nanoparticles synthesized following [3] were applied to the photocatalytic H_2 production reaction, using ethanol as sacrificial agent. It was observed that the synthesized nanoparticles presented activity of 10 times higher than the commercial cerium oxide standard and a better performance than other systems using CeO_{2-x} in the literature. UV-Vis, X-ray Diffraction, X-ray Absorption Spectroscopy, X-ray Photoelectron Spectroscopy, Ultraviolet Photoelectron Spectroscopy and Fourier Transform Infrared measurements were performed aiming to elucidate these results. It was obtained that the small bandgap energy, high surface area and Ce(III) fraction at the surface play a major role on its great performance.

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CNPq, CAPES, LNLS, CNANO.

POSTER PRESENTATION

BREAST CANCER RADIOTHERAPY ENHANCEMENT USING BI_2S_3 NANOPARTICLES

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Cancer is a critical menace to human life, and radiotherapy is one of the most widely employed treatments. However, it has some drawbacks, as lack of specificity and the development of resistance to radiation by tumor cells, which implies an increase in the final dose. There are different approaches to enhance the treatment results and to improve patient recovery. In particular, radiosensitizers provide a novel and simple solution, since they enhance the radiation absorption of cells [1,2]. For this purpose, we synthesized Bi_2S_3 nanoparticles as radiosensitizers for breast tumor cells. We obtained Bi_2S_3 nanorods by the hot injection method using oleylamine as capping agent, which was exchanged for polyvinylpyrrolidone under reflux, to achieve biocompatibility. The nanoparticles were characterized by XRD, IR, and HR-TEM before and after the ligand exchange. The amount of polyvinylpyrrolidone was also determined by TGA-DSC, resulting in a 20% of the total nanoparticles weight. The stability of nanoparticles suspensions in culture medium, fetal bovine serum, and human plasma, was determined by UV-Vis spectrometry, verifying a high stability in all of them. We also performed in-vitro assays in human breast cells MCF7. The cytotoxicity was tested incubating the cells with the nanoparticles during 72 h. The results showed that the Bi_2S_3 nanorods are not cytotoxic up to 2.5 mg/mL. The radiation assays were performed using a 60Co radiation source. A 40% increase in cells death was achieved when a combination of 50µg/mL of nanoparticle concentration and 2 Gy of gamma radiation dose was used instead of only using irradiation. Our results show that Bi_2S_3 nanoparticles could be used as radiosensitizers, which could bring remarkable improvements in radiotherapy treatments, and less secondary effects for the patient.

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KEYWORDS: RADIOSENSITIZER, BI2S3, NANOPARTICLES

POSTER PRESENTATION

CA-AL LDH REGENERATION USING SYNCHROTRON LIGHT SOURCE BY XRD1/D12A AND SAXS/WAXS IN-SITU

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Layered double hydroxides (LDH) are materials represented by the formula $[(M^{2+})_{1-x}(M^{3+})_{x}(OH)_{2}]^{x+}[(A^{-})^{x/n}(zH)_{2}O]$, where M^{2+} and M^{3+} are metal cations, filling up the octahedral interstices of the lamellar layers, whereas A- represents organic or inorganic anions, that are positioned between the layers for load compensation. When dehydrated, LDHs can regain interlamellar structure in the presence of water or anionic solutions. This study investigates Ca-Al LDHs synthetized by mechanochemical process. Those stages may be present in certain commercial cements after use (hydration). Heat treatment of Ca-Al LDH led to the collapse of the layered structure and the formation of mixed oxides. The diffractograms made clear the presence of the LDH structure before calcination and its disappearance after calcination at 400°C. The reformation of calcium aluminates in the presence of water was characterized by means of XRD1/D12A beamline, and the kinetics of rehydration, by means of SAXS/WAXS measurements IN-SITU for 90 minutes. The recovery profile of the structure of the LDHs was observed after the first minutes. The microstructure was observed by scanning electron microscope, providing new information on the morphology of the (re)hydrated compounds. Such rapid regeneration may be beneficial for use in cements in reason of faster consolidation of fluid material, or the provision of mechanical strength in the first days.

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KEYWORDS: LAYERED DOUBLE HYDROXIDES, REHYDRATION, (DE)HYDRATED CALCIUM ALUMINATE, SYNCHROTRON

POSTER PRESENTATION

CHARACTERIZATION OF MONOHYDRATED L-ASPARAGINE CRYSTALS AT 100K BY X-RAY MULTIPLE DIFFRACTION USING SYNCHROTRON RADIATION

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The amino acid crystals are very attractive materials in researches of spectroscopy, crystallography, phase transitions and other correlates [1,2]. It is because these materials have a wide range of potential technological applications on pharmaceutical industry and electronic industry, including electro-optical devices. L-asparagine is one of the 20 protein-forming amino acids, playing a fundamental role in several biological mechanisms. Single crystals of monohydrated L-asparagine $[C_4N_2O_3H_8.H_2O]$ were grown fromaqueous solution by the slow evaporation method at constant temperature. X-ray multiple diffraction technique with synchrotron radiation at low temperature (100 K) was used in the analysis of the monohydrated L-asparagine crystal [3,4]. X-ray multiple diffraction scans were carried out at the XRD2 station of the Brazilian synchrotron radiation facility (LNLS), Campinas, SP, Brazil using l = 1.7066(1) Å. High-resolution azimuthal scans of the (0 8 0) reflection, primary reflection chosen for these experiments. The XRD2 optics is composed by an Rh-coated vertical-focusing mirror and a sagittal-focusing Si 111 double-crystal monochromator. It provides a tunable monochromatic beam ranging from 5 to 15 keV. The X-ray beam with spectral width of 0.0002 and beam divergences of 0.1 mrd was used. The Huber 6 + 2 circles diffractometer with resolution of 0.0002° in all axes and cryojet flow was usid for collect X-ray data at 100 K. It was verified that under low temperature conditions the crystal undergoes a conformational transition.

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KEYWORDS: L-ASPARAGINE, MULTIPLE DIFFRACTION, SYNCHROTRON RADIATION

ORAL PRESENTATION

CLOUD FORMATION DRIVEN BY WATER-SOLUBLE ORGANIC COMPOUNDS PROBED BY XPS

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The distribution and protonation states of amino acids at liquid interfaces (e.g., water droplets surface) is of considerable concern in studies on the formation of clouds in the atmosphere as well as in many biological contexts. In particular, the optical properties of clouds, and therefore their indirect effect on climate, are highly dependent on the number and concentration of cloud condensation nuclei (CCN) in the atmosphere. The presence of surfactant molecules in the atmosphere is known to influence the nucleation process. Amino acids constitute water-soluble organic compounds that can play such a rule. Simulations show that amino acids at surface alter surface tension, an essential parameter for cloud condensation. Therefore it is crucial to access the density of these molecules at the surface. In this presentation, we plan to show that this molecular density at the surface can change substantially depending on the chain length, the attached chemical group [1], and the protonation state of the amino acid, which is generated by the variation of the solution acidity [2,3]. Specifically, study the intricate pH-dependent propensity of amino-acids to the aqueous surface we employ X-ray photoelectron, density functional theory calculations and reactive force field molecular dynamics simulations to study cysteine as a model molecule. Indeed, cysteine in a vital prototype for studies of amino acids since it has three groups: carboxylic (C), amine (N) and sulfuric (S) which may or may not be protonated in aqueous solution. At a specific pH, we will show that ion paring may be behind the unexpected presence of certain protonated species at the surface that are absent in the solution´s bulk.

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KEYWORDS: ELECTRON SPECTROSCOPY, AQUEOUS SOLUTION, AMINO ACIDS

ORAL PRESENTATION

CORRELATION BETWEEN THE ELECTRIC BEHAVIOR AND THE XANES SPECTRA IN $CR_{1.8}TI_{0.2}O_3$

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The Metal Oxide Semiconductors are chemical sensors, which have become mass-use for their large field of applications, their small size and their simple manufacturing. In addition, they have a high sensitivity so they can detect very low concentrations, operate in a wide temperature range and possess long durability. In particular, the system $Cr_{2-x}Ti_xO_3$ is a solid solution with corundum structure ($0.01 < x < 0.45$) and presents promising properties as chemical sensor. The system has a rapid response to gases and VOCs (we studied: acetone, ethanol, isopropyl alcohol and acetic acid). Our XANES studies show that the $Cr_{2-x}Ti_xO_3$ with x= 0.2 (from now on CTO) presents the same spectra than the Cr_2O_3 (at Cr K-edge). Also the studies at Ti K-edge reveal that the CTO contains Ti in III and IV oxidation state. The CTO spectrum, in atmospheric air, could be modeled considering a weighted sum of 35% $Ti(III)_2O_3$ and 65% $Ti(IV)O_2$-rutile spectra. This result confirms the mixture between ions in III and IV oxidation state in CTO, but it disagrees with our XPS results, where we only measured TiIV in the surface. That means that the Ti(IV) is located at the surface of the particle. On the other hand, the CTO has interesting magnetic and electric transport properties. Our studies reveal that the thermal evolution of the conductivity could be modeled by the small polarons model which presents a discontinuity in the curve in the region 750-790K. This is reflected in a variation of the activation energy of the small polarons model. The XRPD patterns of CTO powders, collected at different temperatures, were fitted by the Rietveld method. This analysis allowed us to obtain the thermal evolution of the cell parameters. It is important to emphasize that the cell parameters do not show jumps, as the conductivity curve does. With this result we can discard that the change in the electrical conductivity is associated with structural anomalies. The thermal evolution of the XANES spectra reveals differences between both K-edge data. For the Cr K-edge, the shape of the spectra does not vary with temperature. Instead, analyzing the Ti K-edge, it is noticeable that the spectrum presents a more evident thermal evolution, but without changes in the shape of its peaks. Also in the Ti K-edge, it is appreciable that the evolution of the intensity of the peaks after the edge, related to transitions from 1s to 4p, presents a break in the range 752-796 K. This is the same temperature range where the conductivity shows a change in its conduction mechanism. Finally, if we perform a derivative fit of the XANES spectra we can obtain the weighted amount of $Ti(III)_2O_3$ and $Ti(IV)O_2$-rutile. The variation of each contribution is monotonous and it does not seem to be the origin of the jump in conductivity. The falling in the intensity of the Ti-K XANES spectra of CTO allows us to explain the change of the conductivity mechanism as a consequence of a variation in the electronic environment of the Ti ions.

KEYWORDS: XANES, ELECTRIC TRANSPROT, SMALL POLARONS

ORAL PRESENTATION

DEMANDS ON SYNCHROTRON HIGH ENERGY MATERIALS ENGINEERING BEAMLINE

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The high energy beamlines for materials engineering at SIRIUS will be used for the analysis of bulk metallic samples upon thermomechanical in-situ treatments or ex-situ measurements. Therefore, this type of beamline would help users studying fundamental topics of materials, such as precipitation and phase transformations. The industrial applications can be studied easily in this type of facilities, allowing to simulate heat treatments, industrial fabrication processes, welding, solidification, among others. Finally, new customized experimental setups can be added to this facility, where together with a scientific or industrial partner can be achieved technological and endeavor advancements. These types of facilities are capable of producing results to better understand several microstructural phenomena of different material and fabrication processes. Other topics being recently published in important journals using high energy beamlines are the local atomic structure of thin and ultrathin films. Further examples of relevant scientific engineering issues to be studied at a high energy materials engineering beamline are: in-situ and atomic-scale investigations of the early stages of precipitates and phases, crystallographic texture analysis, lattice defects, element partitioning, intrinsic heat effects on the microstructure, in-situ synchrotron line profile analysis after high-pressure torsion deformation and in-situ investigation of the oxidation behavior of metastable CVD films. The high energy, around 87 kV or higher, allows for working in transmission mode, which provides bulk information in opposition to what occurs during reflection mode geometries, such as at the former XTMS beamline of LNLS. In addition, we consider as high energy, a beam energy capable of analyzing steel samples with a thickness larger than 2 mm, which would contribute with the use of samples representing better the real working conditions. The transmitted signal will be collected in large and fast acquisition detectors/camera. Therefore, high resolution and fast read-out 2D diffraction images will be applied to collect more information within a few seconds regarding microstructural and physical phenomena. We recommend to include a tensile and compression machine, a quenching and deformation dilatometer, a torsional test machine, a fast-displacement system to acquire measurements in different sample locations, and a fast acquisition detector for fast microstructural transformation studies.

KEYWORDS: HIGH ENERGY BEAMLINES, MATERIALS ENGINEERING, IN-SITU AND EX-SITU MEASUREMENTS, BULK METALLIC SAMPLES

Poster Presentation

DESIGNING A MODULAR SAMPLING SYSTEM FOR SOIL-RHIZOSPHERE ANALYSIS ON THE CARNAÚBA AND MOGNO BEAMLINES

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The need for increased food production to meet the demand of a growing worldwide population will require more efficient delivery of nutrients from soils to plants. The Carnaúba and Mogno beamline groups are developing a “rhizobox” system for *in-situ*, high-resolution imaging of time-varying processes at the root-rhizosphere-soil interface. The rhizosphere is a unique zone between plant roots and bulk soil where root exudates and greater soil microbial activity strongly influence biogeochemical processes. Our rhizobox will be a modular system that can accommodate a variety of specific experiments requiring isolation of microns- to millimeter-sized roots for imaging rhizosphere processes in 2D (e.g., µ-XRF mapping and spectroscopy) or 3D (fluorescence and transmission tomography). The system is being designed to be compatible with both the Carnaúba and Mogno beamlines to facilitate imaging at different length scales, ranging from centimeters to submicron. The system under consideration comprises a modular, soil-filled pot that will attach to the stages at both beamlines, with root receptacles (e.g., capillaries) attached below the pot for isolating one or more live roots in soil. Constraints include a weight restriction for the load capacity of the piezo stage on Carnaúba, and the need to create realistic soil conditions that promote root growth into isolated receptacles. Thin, X-ray transparent windows will be placed at one or more locations along the length of the receptacle for measuring movement, speciation, and root uptake of multiple chemical elements over time. This system will help agricultural and environmental scientists gain deeper knowledge about the dynamics of (sub)micron-scale processes controlling the efficiency of plant acquisition of nutrients, and also uptake of soil contaminants.

POSTER PRESENTATION

DEVELOPMENT AND ELECTROCHEMICAL BEHAVIOR OF A VERSATILE SPECTROELECTROCHEMICAL CELL FOR IN-SITU EXPERIMENTS IN ELECTROCHEMISTRY

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Electrochemical processes are involved in many fields of science and technology as they directly impact the sectors of energy (batteries, supercapacitors, etc.), health (electrochemical sensors), environment (water treatment, biomass conversion, etc.), among others. The rational development of materials for electrodes requires of a deep knowledge of the process that occurs in the electrode-solution interface. Thus, the use of spectroscopic techniques coupled to electrochemistry, are mandatory in order to get information about these processes. The development of versatile, cheap and easy to build spectroelectrochemical cells (SEC) contribute to the progress of the field of electrochemistry and its impact in science and technology. Therefore, in this work, we describe in detail the development of a SEC that can be used for several IN-SITU techniques (FTIR, Raman, XAS, XRD and some using femtosecond lasers, among others) just by changing commercially available windows. Different to most of the contributions in the literature, we carefully analyze the electrochemical response of the SEC, which must be the same than the obtained in a electrochemical system. Otherwise, the spectroscopic data can only be connected with the electrochemical results obtained only in the SEC.

KEYWORDS: ELECTROCHEMISTRY, IN-SITU, XAFS, XRD

POSTER PRESENTATION

DEVELOPMENT OF A CHEMICAL STAINING PROTOCOL TO STUDY *RHODINIUS PROLIXUS* STRUCTURES BY SYNCHROTRON MICROTOMOGRAPHY

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Synchrotron microtomography has already shown to be a powerful tool for studying insects' morphology yielding images with high resolution, in a non-destructive way and with fast data acquisition [1-2]. Biological samples such as insects usually require the use of X-ray absorbing contrast agents in sample preparation, as there is a very little difference in the attenuation coefficient among soft tissue types. In the present work, we used different combinations of fixatives and staining so that contrast and visualization of details of the soft tissues of Rhodnius prolixus could be improved. Rhodnius prolixus is a model organism for the study of cellular and physiological processes in insects, and the main insect vector of Tripanosoma cruzi, the etiologic agent of Chagas disease, which accounts for 8,000 deaths in 2015, affecting mainly Latin American. The results were compared using image quality parameters (contrast and signal-to-noise ratio) and using longitudinal sections of Rhodnius prolixus head. All the samples were measured using the IMX imaging beamline at LNLS. The fixative/staining combinations used were Bouin's Fluid + Osmium tetroxide (Bouin + Osmium), Bouin's Fluid + Iodine (Bouin + Iodine), Glutaraldehyde +Osmium tetroxide (Glut + Osmium), Glutaraldehyde + Phosphotungstic acid (Glut + PTA) and in addition the control samples, without any type of staining, Bouin's Fluid (Bouin) and Glutaraldehyde (Glut). In this work, we demonstrate that appropriate sample staining with chemical agents is a simple way of increasing the contrast of relevant low-absorbing structures present in the specimen. The results have shown that the best fixative/staining combination for these insects' samples is Bouin + Iodine. The reported result shows that only a few staining methods for Synchrotron Radiation Phase Contrast Microtomography demonstrated to be a valid tool for increasing the contrast in insects.

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KEYWORDS: RHODINIUS PROLIXUS, MICROTOMOGRAPHY, STAINING

POSTER PRESENTATION

DEVELOPMENT OF A DOUBLE CRYSTAL DEFLECTION SYSTEM FOR XRR MEASUMENTS OF LIQUID INTERFACES ON SAGUI BEAMLINE AT SIRIUS

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X-Ray Scattering, Diffraction and Reflectivity studies of liquid interfaces are becoming well established at Synchrotron Light Sources, allowing IN-SITU characterization of atomic and molecular structures with a great impact in many fields, such as electronics, and pharmaceutical/food industries. It also has a great appeal in pure sciences, providing a practical understanding of phase transitions in quasi-2D systems and surfactants behaviors [1]. However, the (horizontal) liquid interfaces present a challenging problem due to the inability of tilting neither the sample surface nor the source, in order to achieve the incident angle variation, required by the techniques. In this scenario, a few specialized instrumentations have been developed to deflect the incoming beam onto the sample surface with high precision. The first designs presented an additional crystal or mirror at the end of the optics setup, used to tilt the primary beam onto the sample surface. In the former case, the beam moves both vertically and horizontally at the sample when varying the incidence angle, which requires the sample and detector to track the moving X-ray, bringing mechanical instability to the surface [2]. In the mirror case, although the experiment is much more stable, the setup does not allow a reflectivity experiment. A deflecting mirror system is currently available for use at the XRD2 beamline at UVX. In this work, we present the design and development of an alternative deflecting system, in which the liquid surface stays stationary over the whole angular variation. The system, called by "deflector", uses two crystals in a DCM configuration, each one in a different Bragg condition (e.g. Ge 111 and Ge 220 reflections) [3]. The sequential Bragg reflections, combined with the rotation of the deflector along the primary beam axis, allows the incident angle at the surface to be changed, while the measuring position remains centered and stationary at the sample surface. Similar designs were implemented on beamlines ID10 and ID15 at ESRF, P08 at PETRA III and I07 at DIAMOND [4]. This is a new design that accounts for the particular requirements of the XRD2 at UVX and future SAGUI beamline at Sirius. The greatest advantage of this system is that it is designed to perfectly fit the existing 6+2 circle diffractometer of the XRD2/SAGUI beamlines, in a way that it can conveniently be used for Grazing Incidence X-ray Diffraction (GIXD) and Grazing Incidence Small Angle X-ray Scattering (GISAXS) in combination with the XRR measurements.

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KEYWORDS: INSTRUMENTATION, XRR, LIQUID INTERFACES, LANGMUIR TROUGH

POSTER PRESENTATION

DEVELOPMENT OF ADVANCED TECHNIQUES AT CARNAÚBA BEAMLINE OF SIRIUS FOR ENVIRONMENTAL SCIENCE AND NANOTOXICOLOGY RESEARCH

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Engineered nanomaterials (ENMs) were designed and produced to have at least one dimension of 100 nm or less. Due to their unusual chemical, mechanical, electrical, optical, and/or magnetic properties, ENMs have been applied in structural engineering, electronics, optics, alternative energy, environmental remediation and medical services [1,2]. Nowadays, safety concerns about ENMs have increased due to the possible adverse effects on biological and environmental systems. This leads the emergence of nanotoxicity, which needs to be assessed and addressed [1, 2]. Nanotoxicology is an emerging discipline that can be known as the science of engineering nanodevices and nanostructures that deal with their effects on living organisms and the environment. The progress of this new area of knowledge, depends mainly on the development of a methodology to characterize nanomaterials in biological samples, quantify nanoparticles in living systems and study their uptake, translocation, biodistribution, location and chemical status in vitro and in vivo [1,2]. The potential toxicity of ENMs to aquatic organisms is a matter of interest since increased commercialization will inevitably lead to some instances of inadvertent environmental exposures. Guidelines for the ecological toxicity testing of ENMs were identified as a priority goal by the OECD. For instance, ENMs exposure in Daphnia magna (an aquatic invertebrate which is the most commonly used test organism in ecotoxicological studies) could be performed according the OECD Guidance [3]. To study the potential toxicological effects in aquatic organism and the assimilation and spatial distribution of ENMs in D. magna, we propose the use of CARNAÚBA beamline at Sirius. The new Brazilian fourth generation light source Sirius represents nowadays one of the most modern SR sources capable of studying several kinds of materials with unprecedent brilliance. CARNAÚBA (Coherent XRAy Nanoprobe BeAmline) is the longest among Sirius first phase beamlines with 145 m from source to the sample. It will cover an energy range from 2 to 14 keV, accessing the K-edges of lighter elements such as P and S. Multiple techniques such as, X-ray fluorescence, X-ray absorption, X-ray diffraction and advanced X-ray coherent methods can be possible to use and combine to understand the local properties of heterogenous material at a nanometer range [4]. Recent technological advances in X-ray focusing optics and fluorescence detection have greatly improved the use of SR techniques for environmental science and nanotoxicology research. For that purpose, we considered that both the developed of analytical techniques at CARNAUBA beamline and the innovative facilities of Sirius, would provide a powerful mean for characterizing the toxic, biological and environmental behaviors of ENMs.

KEYWORDS: SYNCHROTRON RADIATION, NANOTOXICOLOGY, NANOMATERIALS, SIRIUS

ORAL PRESENTATION

DIFFRACTION STUDY OF QUANTUM CRITICALITY IN THE CHARGE DENSITY WAVE SYSTEM LU(PT$_{1-X}$PD$_{X}$)$_{2}$IN

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Quantum phase transitions have been intensively studied in condensed matter physics. Over the recent years, many systems were shown to present an ordered state that can be suppressed by external parameters leading to a quantum critical point (QCP). Investigations on systems with charge ordered QCPs are, however, still scarce. In this work we study the charge density wave (CDW)/superconducting Lu(Pt$_{1-x}$Pd$_{x}$)$_{2}$In material. This compound has a QCP close to $x_c \sim 0.58$ of Pd content, where the CDW state vanishes and superconductivity is enhanced [1]. Using synchrotron x-ray diffraction we investigate the CDW scattering peak as function of temperature and Pd content. We observe the presence of quantum fluctuations (QF's) effects over the classical CDW phase transition by mapping the charge order parameter critical exponent (β) near the QCP. Due to the QF's, the exponent β approaches the value predicted by mean-field theory and it might be related with a dimensional crossover.

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KEYWORDS: QUANTUM PHASE TRANSITIONS, CHARGE DENSITY WAVES, X-RAY DIFFRACTION

POSTER PRESENTATION

ELECTRONIC STRUCTURE OF THE SUPERCONDUCTING COMPOUND $SRTIO_3$-DELTA

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The insulating $SrTiO_3$ (STO) compound is well known for its ferroelectricity [1], large dielectric constant [1] and superconductivity [2] at very low temperature. But the presence of oxygen vacancies in STO may lead to very different physical properties. For example, non stoichiometric STO goes through a metal-insulator transition, and it was recently shown that has interesting thermoelectric properties [3]. To fully understand the effects of the vacancies on the electronic structure of STO, we have performed photoemission (PES) spectroscopy and Ti L3 resonant photoemission (RPES) on $SrTiO_3$-delta single crystals, in the low oxygen vacancy concentration limit. All the experiments were carried out at the PGM beamline (LNLS). The PES and RPES measurements were performed at room temperature, and with a photon energy of 103 eV and around 450 eV, respectively. The experimental spectra were also compared to band structure calculations. The results show that the O 2p part of the valence band of STO is sensitive to oxygen vacancy concentration and, for higher levels of oxygen vacancies, there is an apparent anisotropy in chemical bonds. The RPES measurements on Ti L3 edge show that there is a significant Ti 3d contribution to the O 2p band energy region, and the Ti 3d - O 2p interaction is also affected by the oxygen vacancy concentration. Finally, the band structure calculations show an asymmetric charge distribution near the oxygen vacancy due to the distortion of atomic positions.

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KEYWORDS: ELECTRONIC STRUCTURE, X-RAY SPECTROSCOPY, DFT

POSTER PRESENTATION

ELEMENT DETERMINATION AND SULFUR CHEMICAL SPECIATION IN PLANTS USING XRF AND NEXAFS: THE ANDIRA SURAMINENSIS CASE

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The inorganic composition (macro and micronutrients) plays a very important role in a plant metabolism. Using the X-ray fluorescence technique, both employing a conventional X-ray source source and synchrotron radiation, we have recently [1] been able to determine and quantify the presence of magnesium, aluminum, silicon, phosphorous, sulfur, chlorine, potassium, manganese, iron, copper, zinc, strontium and barium in the leaf and in the bark of a plant from the Amazon rainforest, Andira surinamensis. It was observed for instance that while some elements , such as sulfur and chlorine, are present in higher concentrations in the leaf, the inverse situation occurs for calcium, which is present in larger concentration in the bark. These results have also been confirmed using an ion beam technique, Rutherford Backscattering Spectrometry (RBS). The chemical ambiance surround the sulfur atom was examined in more detail using the Near Edge X-ray Absorption Spectroscopy (NEXAFS) technique [2]. This chemical speciation has shown that sulfur is present in this plant in several oxidation states, with a much larger contribution from the inorganic sulfate in the leaves. A rigorous data treatment procedure was adopted, based on the use of Principal Components Analysis, Target Transformation and Linear Combination Fitting methodologies. The procedure was validated by performing the analysis of mixtures of standards with known composition and submitting the experimental results to the same data treatment [1].

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KEYWORDS: WD-XRF, SR-XRF, RBS, XANES, ANDIRA SURINAMENSIS

POSTER PRESENTATION

ELEMENTAL MAPPING OF A LARGE REGION OF A WORK OF ART THROUGH SYNCHROTRON LIGHT

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In this work, a work of art, of unknown authorship, supposedly dated from the seventeenth century and which belongs to the collection of the Museum of Fine Arts School of the Federal University of Rio de Janeiro, was analyzed by synchrotron light in the line of micro X-Rays Fluorescence, from the Brazilian Synchrotron Light Laboratory (LNLS), located in Campinas, São Paulo. The painting had a total area of 150 mm x 150 mm analyzed, having been measured four quadrants of dimensions 80 mm x 80 mm. The analyzes were performed using the voltage at 20 keV, the beam collimated at 100 µm and each pixel acquired during 100 ms, totaling a measurement time of 5 days, counting the manual adjustments of positioning. The data cubes were analyzed using the PyMca software, where it was possible to perform fit models of the spectra of XRF sum of each quadrant and reconstruction of the image of each element, present in the fit model. In all the spectra sum of each quadrant, the elements Ca, Fe, Ba, Zn, Pb and Hg were detected. Through the elementals maps it was possible to verify that Pb is present in the whole analyzed region, being this element associated with pigments as lead white [$2PbCO_3.Pb(OH)_2$] and/or yellow Massicot [PbO], commonly used in the preparation layer of historical paints, due to the secant and sealant properties of Pb. The Fe elemental map reveals that it is associated with black pigments, with Fe being associated with the magnetite [Fe_3O_4] pigment, being this pigment only has its registered use from the 19th century, so the extensive use of this black pigment is an indicative, which work of art is anachronistic, as its dating period 17th century. The Zn elemental map, associated with the white regions, is also another indication that the painting is not from the dating period, since the Zn is the key element of the zinc white [ZnO] pigment, which began to be used in the century XIX. In one of the quadrants, was carried out elemental mapping of a region, which consisted of a signature is not very visible , which can be associated to the author of the painting, being that the Ca elemental map this region revealed a signature that referred to the painter Spanish Diego Velázquez, who died in the 17th century. Despite the signature of a famous painter, the pigments detected in the analyses as magnetite and zinc white, are indications that the work of art studies in this work, is later than the 19th century and a possible imitation of the style of the Spanish painter Diego Velázquez. This study indicates the efficacy of the results obtained by elemental mapping of large areas in works of art, which allows us to evaluate the creative process employed by the artist. However, the technique also has a great potential for performing forensic studies in art works.

KEYWORDS: ELEMENTAL MAPPING BY XRF; HISTORICAL PIGMENTS; XRF DATA PROCESSING

POSTER PRESENTATION

ENERGETIC PROCESSING OF NITRILE-BEARING ICES BY ULTRAVIOLET AND X-RAYS RADIATION

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Nitriles represent a quite abundant class of molecules in a variety of astrophysical environments. Acetonitrile (CH_3CN), propionitrile (C_2H_5CN) and acrylonitrile (C_2H_3CN) are common examples of saturated and unsaturated organic nitriles present in dark clouds [1] and star-forming regions [2], while isobutyronitrile (i-C_3H_7CN) was the first branched molecule to be detected in the interstellar medium (ISM) [3]. Noteworthy, CH_3CN is a known cometary molecule, and it has been recently detected towards the V4046 Sgr, MWC 480, and HD 163296 protoplanetary disks [4], what points to the link between the interstellar and nascent planetary systems. However, the reaction routes for producing and destroying such complex molecules are not understood. At temperatures as low as 10 K, gas-phase molecules are expected to condense on dust particles, forming ice mantles. In the case of protoplanetary disks, these ices are exposed to the stellar radiation field from hot young stars, mainly in the far ultraviolet and soft X-ray energy range, what triggers the energetic processing of condensed molecules. In order to estimate the photostability of condensed organic nitriles, we derived the cross-sections for destruction of the parent molecules under conditions that mimic those found in the ISM. The experiments were performed at the SGM beamline at the Brazilian synchrotron laboratory (LNLS). The ices were grown in the multilayer regime, IN-SITU, onto a gold foil substrate cooled at 15 K. Each of these ices was exposed to different doses of zero order synchrotron radiation, and the damage induced after each irradiation was probed by the Near Edge X-ray Absorption Fine Structure (NEXAFS) technique at the N K-edge in the total electron yield (TEY) detection mode. As a general trend, it was observed the decrease of the $N1s \rightarrow \pi^*(CN)$ excitation at ~399 eV, and its splitting into three main components, due to the different chemical environment of the irradiated ices. The two new spectral features appeared around ~398 and ~401 eV. This result might indicate the synthesis of imine-based compounds (R–C=C=NH) from nitrile-bearing ices exposed to UV and X-ray radiation, corroborating that the abundance of imines, such as the known interstellar ketenimine (CH_2CNH), might be correlated to the abundance of nitriles. Cross-sections for the destruction of the parent molecule were derived from the integrated resonance as a function of the photon exposure. The extrapolation to the typical X-ray photon flux from young stellar objects indicates that nitriles should be processed within the first millions of years of activity of the central protostellar. We hope that these parameters may aid in the developing of chemical evolution models of nitrile rich environments in the ISM.

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KEYWORDS: NITRILES, NEXAFS SPECTROSCOPY, ASTROPHYSICAL ICES, LABORATORY ASTROPHYSICS

POSTER PRESENTATION

ENHANCING THE CHARGE-GENERATION PERFORMANCE OF POLYSILAFLUORENE-DERIVATIVE FILMS BY INTRODUCING A LOW-COST SENSITIZER

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The strategy of using semiconductor materials with different properties as electron donor materials in organic solar cells (OSC) is used to improve absorption, stability or charge generation. In this work, it is investigated the effect of a silafluorene derivative copolymer, the poly[2,7-(9,9-dioctyldibenzosilole)-alt-4,7-bis(thiophene-2-yl)benzo-2,1,3-thiadiazole] (PSiF-DBT), sensitized by a low-cost homopolymer from PPV (polyparaphenylene vinylene) family, the poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV). The interaction between the two donor (neat and in a blend) polymers films was evaluated by ultraviolet-visible, photoluminescence, X-ray photoabsorption (NEXAFS) spectroscopies, atomic force microscopy (AFM) and correlated to the observed in photovoltaic performance. We studied the mixture as active layer in two device's geometries - considering bi-layer devices with a fullerene derivative and inverted flexible devices blade coated in air conditions with a non-fullerene small molecule acceptor. Also, resonant Auger spectroscopy using the core-hole clock (CHC) method [1] was employed in order to evaluate the ultrafast charge delocalization times of conjugated polymers in the low-femtosecond regime [2]. The results show that the homopolymer can improve the absorption spectra and the nonradiative-energy transfer from it to silafluorene derivative copolymer acts as a photosensitizer in the copolymer units. In addition, the blend film exhibits an organized morphology resulting in better absorption stability than the neat films when kept under continuous illumination.

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KEYWORDS: ORGANIC SOLAR CELLS, TWO ELECTRON DONORS, LOW-COST SENSITIZER, NEXAFS, ULTRAFAST CHARGE TRANSFER, LIGHT STABILITY

POSTER PRESENTATION

EVALUATION OF IMAGE QUALITY PARAMETERS IN SYNCHROTRON FAST MICROTOMOGRAPHY OF BIOLOGICAL SAMPLES

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Conventional tomography or microtomography are well-established techniques to study biological specimens that provides information on the two-dimensional (2D) and three-dimensional (3D) microstructure. The main parameters affecting the speed of the microtomography data collection are the photon flux, the detector efficiency, the detector readout time and the architecture of the data acquisition system [1]. Technological advances in detectors and algorithms, that emerged to improve the image quality, are important to reduce scan time consumption and therefore, reduce the delivered dose while keeping a better image [2]. Reduce the number of projections is an option to decrease tomography scan time, however limiting the spatial resolution that can be achieved. We have performed our measurements at the Brazilian Synchrotron Laboratory IMX beamline. The sample was scanned over 180° with 1000 projections, 650 ms exposure time, 4,11 µm pixel size and operating in white beam mode increase flux in the sample, thus reducing scan time. The reconstructions were carried out using the open-source software SYRMEP Tomo Project (STP) [3]. In this work, a quantitative image quality study was carried out comparing filtered backprojection (FBP), Simultaneous Iterative Reconstruction Technique (SIRT), Simulaneous Algebraic reconstruction Reconstruction Technique (SART), applying phase retrieval and using different number of projections for image reconstruction. In this work we used the crystallin lens of the tadpole Thoropa miliaris to study the alteration caused by application of three different algorithms and the impact in the image quality. Reduction in the number of projections using FBP algorithm results in a significant loss in the image quality and as consequence loss of precision in volumes quantification. The use of interactive methods results in a smaller loss even though the time for the reconstruction is relatively longer. All used algorithms are implemented in STP. We evaluate also Signal-to-Noise Ratio (SNR) and Constrast-to-Noise Ratio (CNR) parameters. Future experiments will remain to carry out very fast tomography scans keeping a good image quality with the lowest radiation dose possible considering the features proposed to MOGNO beamline at Sirius synchrotron facility.

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KEYWORDS: SYNCHROTRON, MICROTOMOGRAPHY, BIOLOGY

POSTER PRESENTATION

EVALUATION OF METHYL ORANGE DEGRADATION MECHANISM WITH SNS_2 PHOTOCATALYTIC NANOPARTICLES

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Chemical contamination of water resources is a global concern. Some of the contaminants we can find are dyes, metals, agrochemicals and other organic compounds. Many strategies are studied to reverse or not worsen this situation. Among the studied solutions, heterogeneous photocatalysis performed by nanoparticle semiconductors is one of the most promising ones. The most common studied and employed photocatalyst is TiO_2, but it has the disadvantage of absorbing light in the UV region [1]. Tin sulfide (IV) nanoparticles are studied for their excellent properties as: absorption in the visible region (Eg 2.2- 2.4 eV), easy and low cost synthesis method, stability and low toxicity [2]. With the aim to study SnS_2 as an agrochemical compound photocatalyst, we obtained SnS_2 nanoparticles by a hydrothermal procedure. Hexagonal and rounded nanoparticles of hexagonal crystalline phase of SnS_2 were obtained and tested as photocatalysts. We selected Methyl Orange (MO) as a model to study the degradation mechanism. We studied the effect of MO concentration on the photocatalytic process and compared our results with TiO_2 P25. For a MO concentration of 2.5×10^{-5} M, SnS_2 showed a higher rate of degradation compared to TiO_2, $KappSnS_2 = 0.02894$ $KappTiO_2 = 0.01028$, respectively. This result is attributed to a more efficient absorption of SnS_2 nanoparticles and to the smaller nanoparticle size, which leads to a better electron-hole separation than in TiO_2. SnS_2 recovery after 3 photocatalytic cycles was evaluated. We observed the formation of SnS_2 with the increased cycle number, which was lately avoided employing a washing procedure with H_2O and Ethanol. Additionally, using UV-Vis spectroscopy analysis, we proved that MO degradation by SnS_2 begins with a direct reduction of the azo bond. Evidence that the secondary analytes remain after the complete reduction of the azo bonds was also proved. The UV absorption maximum of these analytes correspond to the sulfanilic acid and N, N-dimethyl-p-phenylenediamine. Structural elucidation using HPLC-MS/MS studies were performed in order to confirm these analytes. Our results show that SnS_2 is a selective photocatalyst that should be potentiated through the development of heterostructures with capacity to completely mineralize organic compounds.

KEYWORDS: SNS2, PHOTOCATALYSIS, DEGRADATION MECHANISM

POSTER PRESENTATION

EVALUATION OF THE EQUILIBRIUM STATE AND STRUCTURE OF COACERVATES FORMED BY COPOLYMERS-IN-BLOCK AND OPPOSITELY CHARGED POLYMERS

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The literature describes many studies on complex systems formed by the interaction of oppositele-charged species in solution, which undergo coacervation [1-2]. These coacervates may be formed by the combination of two polyelectrolytes with different charges, or polyelectrolytes and ionic surfactants, as well as involving block-copolymers, consisting of hydrophilic and ionic parts with charged species with opposite charges [3], [4]. However, it is still unclear whether or in which conditions these structures represent equilibrium systems. In other words, situations in which morphology, phase size, composition, etc., of the structures are no longer dependent on the preparation procedure and aging. This is the central point that is investigated in this project. For this, coacervates consisting of copolymers containing a hydrophilic neutral block and another anionic, such as polyacrylamide-b-poly(acrylic acid), (PAmx-b-PAAy) and poly(ethylene oxide)-b-poly(acrylic acid), (PEOx-b-PAAy), which are neutralized by the polycation poly(diallyldimethylammonium chloride), PDADMAC of different molar masses. To achieve these objectives, the systems were prepared in different concentration of the components, by using different protocols. Based on the recent results, it is still inconclusive whether or not the complexes are in an equilibrium state. Concerning the structure of the complexes (concentrated systems), they were characterized by using, light scattering measurements (DLS and SLS) and low-angle X-ray scattering (SAXS). From SAXS results, it was verified small signs of crystalline structure that is formed in two length scales, in the more concentrated mixtures of these complexes.

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KEYWORDS: COACERVATES, POLYELECTROLYTE, SAXS

Poster Presentation

EVOLUTION OF SIZE AND COMPOSITION OF COPPER ANTIMONY SULFIDE NANOPARTICLES IN THE HOT INJECTION SYNTHESIS

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The mechanism that governs the formation of copper antimony sulfide nanoparticles obtained by hot injection method was studied. The synthetic procedure was the following: in a three neck flask, 0.45 mmol of CuCl, 0.45 mmol of $SbCl_3$, and 7 mL of oleylamine were added. The solution was degassed at 80°C and heated, under nitrogen atmosphere, to the reaction temperature (200 to 250°C). In another flask, 1 mmol of sulfur in 3 mL of oleylamine was heated to 60°C and stirred until a translucid, reddish solution was observed. The sulfur solution was injected on the three neck flask, starting the reaction. To monitor the nucleation/growth of the particles, aliquotes were taken at 1, 2, 5, and 10 minutes of reaction. The samples were characterized by UV-Vis-NIR absorption spectroscopy, Raman spectroscopy, X-ray diffractometry, small angle X-ray scattering, and transmission electron microscopy. The analysis of the X-ray diffraction patterns and the Raman spectra showed clearly the formation of copper thioantimonate (Cu_3SbS_4) and copper thioantimonide ($CuSbS_2$) in all the studied temperatures. In all temperatures, it was observed the formation of Cu_3SbS_4 after one minute of reaction and its transformation to $CuSbS_2$. The kinectics involved in this transformation is temperature-dependent: it ocurred between 5 and 10 minutes in lower temperatures, such as 200°C and between 1 and 2 minutes in higher temperatures, like 240 and 250°C. To confirm the last suggested step, an experiment where the Cu_3SbS_4 nanoparticles were used as precursor, alongside oleylamine and SbCl3 at 200°C was performed. In the same way as the previous experiments, the sulfur solution was injected on the three-neck flask and the reaction was kept for 9 minutes until quenched by cooling down. The sample was characterized by XRD, indicating the presence of $CuSbS_2$, confirming the sugestion of conversion from Cu_3SbS_4 to $CuSbS_2$. The size evolution of the nanoparticles was followed by TEM and SAXS. The objective is to determine if the Cu_3SbS_4-$CuSbS_2$ conversion is caused by a dissolution of the Cu_3SbS_4 and reassemble into $CuSbS_2$ nanoparticles or the conversion of a whole existent particle from one compound to another. Determining this dynamics will be a decisive step in order to design the copper-antimony chalcogenide-based nanoparticle synthesis.

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Keywords: Copper antimony sulfide, Hot injection, Nanoparticles

POSTER PRESENTATION

EXAFS ANALYSIS OF STRUCTURAL DISORDER IN THE $CO_3O_2BO_3$ LUDWIGITE

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Homometallic ludwigites with chemical formula $((M^{2+})_2(M^{3+}))O_2BO_3$ are mixed-valent complex oxides with potentially interesting physical phenomena. It was recently shown that a hybrid of reduced-multiwalled carbon nanotubes and $Co_3O_2BO_3$ have outstanding performance as an oxygen evolution reaction (OER) electrocatalyst, where the slow OER kinetics presents the main bottleneck regarding the storage of renewable energy and clean energy generation [1]. The novel catalyst containing $Co_3O_2BO_3$ have an overpontential lower than that for the state of the art RuO_2 catalyst [2]. The remarkable OER electrocatalyst performance of the ludwigite was mainly attributed to its local distorted octahedral environment, which increases the unit cell volume and enhance its catalytic active surface area. In addition to that, atomic positional disorder may play a significant role in the Co ludwigite unit cells volume size. However, the possibility of structural disorder in $Co_3O_2BO_3$ lacks a dedicated study in contrast to other heterometallic ludwigites, which are known to present disordered structures [3]. Finally, understanding the role of structural disorder in these materials may help the synthesis of robuster and more efficient OER electrocatalyst for green energy production. This work investigates structural disorder in $Co_3O_2BO_3$ as a function of temperature by applying reverse Monte Carlo (RMC) methods in EXAFS data analysis. The EXAFS spectra was extracted using traditional methods [4] from Co K edge X-ray absorption spectroscopy experiments performed at the XAFS2 beamline of LNLS. Then, RMC methods were applied to refine the Co ludwigite atomic position by introducing random small amounts of disorder in the system until the refined crystal structure EXAFS sprectrum reproduces experimental data. In addition to that, the convergence in reasonable time of simulated results depends upon the use of a evolutionary algorithm (EA), which allows us to cover a much bigger area of the configurational space much faster than regular methods. The EXAFS-RMC/EA analysis was performed using EvAX (Evolutionary Algorithms for XAS analysis) [5]. In this work we will show experimental and simulated EXAFS for $Co_3O_2BO_3$ for various temperatures from 20 to 850 K. The structural disorder of the Co ludwigite will be on focus. In addition to that, the broad temperature range enables us to investigate the influence of physical phenomena in the EXAFS spectra as well as their influence on disorder. Particularly, $Co_3O_2BO_3$ presents two charge ordering transition and a spin-state crossover within this temperature range.

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KEYWORDS: EXAFS, LUDWIGITE, MONTE CARLO

POSTER PRESENTATION

EXPERIMENTAL AND THEORETICAL CHARACTERIZATION OF KAOLINITE BY DFT, XANES *AB INITIO* SIMULATIONS, AL K XANES AND SI K XANES/EXAFS

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Kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$) is classified as a 1:1 dioctahedral phyllosilicate and it is the main component of the kaolin group of minerals. The importance of kaolinitic clays in the development of modern ceramic science can best be appreciated by considering its widespread influence on ceramic, material science, and mineralogy. These clays have been widely used in different technological applications for thousands of years [1]. Its technological importance requires an exhaustive study of its morphological nature as an electronic structure. In a recent paper [2] a detailed first principles study of the bulk structure of kaolinite was carried out, and the predictions solve previous controversies around kaolinite bulk structure. In this work we extend the theoretical aspects, to introduce the structures generated by DFT-calculus in the FEFF, FDMNES and SPR-KKR programs to simulate the absorption spectra in the K edge of the Al and Si, correlating these results with the experimental data obtained in the SXS-beamline (LNLS, Campinas, SP, Brazil). In addition, Si K EXAFS spectra were obtained for kaolinites with different degrees of crystallinity and distortions. This allows to make adjustments of the EXAFS signal and its corresponding Fourier transform, and compare with the models obtained by DFT. In this meeting we present the advances of this research.

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KEYWORDS: KAOLINITE, DFT, XANES-SIMULATIONS, EXPERIMENTAL XANES/EXAFS

POSTER PRESENTATION

EXPLORING NANOSTRUCTURED SEMICONDUCTORS FOR PHOTOVOLTAIC DEVICES

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Nanomaterials as nanostructures have promising potency to enhance the performance for solar cells. Those nanostructures have quantic confinement suitable to be manipulated to absorb radiation in a width range of the electromagnetic spectrum [1]. In particular, among different nanosemiconductors (NS) materials, atomic quantic clusters (AQCs) appear as good candidates to absorb radiation and generate photocurrent, mostly because it is possible to tailor the band gap to efficiently absorb in the visible region [2]. Additionally, traditional solar cells use transparent conductor electrodes of Tin Indium Oxide (ITO). These oxides have some restrictions as: limited sources of indium, susceptibility to ionic diffusion in polymeric structures, chemical instability and fragility. Some alternatives to replace ITO can be explored using graphene based materials, such as graphene oxide (GO) and reduced graphene oxide (rGO). Because their electrical properties, chemical and mechanical stability, GO and rGO become an excellent candidate for prototypes of photovoltaic devices. In this work we present and characterize different versions of prototypes of photovoltaic devices employing Cu5 AQC and Cu5 ACQ on TiO_2 as semiconductor nanomaterials, among others for comparison. Samples with substrates of rGO/ITO and rGO/Si where also employed. Photo-electrochemistry studies were performed to determine photocurrent values, showing its increment with the addition of Cu5-AQCs on different substrates. Cu5-AQCs were characterized by Cu-K XANES spectroscopy at the XAFS2 beamline at the Brazilian Synchrotron Light Laboratory (LNLS, Campinas, Brazil).

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KEYWORDS: NANOMATERIALS, PHOTOVOLTAICS, CLUSTERS

POSTER PRESENTATION

EXPRESSION OF METHYLTRANSFERASES HTRM9L AND TRM112 FROM *HOMO SAPIENS* FOR FUTURE STRUCTURE SOLUTION

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Transporter RNA (tRNA) takes part on the fundamental process of protein synthesis. Its function is to transport aminoacids that will be used during protein synthesis in the ribosome. For this task to be accomplished correctly, many tRNA molecules need chemical modifications, like some nucleoside methylation, to assure their correct folding and its correct decodification1. The methylation process is performed by enzymes called methyltransferases (Trm) and uses S-adenosy -methionine (SAM or AdoMet) as a methyl group donor2. The complex Trm9/Trm112 (in which Trm9 is the de facto methyltransferase and Trm112 is an auxiliary subunity) is conserved in eukaryotes and Trm9 presents two ortologues in humans, namely, ABH8 e hTrm9L. This work aims at expressing human hTrm9L and Trm112 heterologously for future structure solution. *Escherichia coli* BL21(DE3) cells were transformed by electroporation with plasmids pET21b(+) that harbored the coding genes of which subunit. Cells that were effectively transformed were selected by growth in media supplemented with ampicillin. Subsequently, transformed cells were propagated in 5 mL of liquid medium ZYP-5052 (with a composition to specifically express the proteins through self induction)3 at 37°C for 22 h. Media were centrifuged and cells were promptly resuspended in lysis buffer (20 mM Tris-HCl, 200 mM NaCl, pH = 7.5); they were sonicated for 5 min. The resulting suspension was centrifuged to separate the cell debris. Samples from total lysis fraction and of the soluble and insoluble fractions were taken for analysis by SDS-PAGE. A Ni^{2+} affinity chromatography of the total lysed fraction was also accomplished. The SDS-PAGE results from expression tests of the Trm112 protein indicated an intense band in the expected position for molecular mass of circa 14 kDa (theoretical mass 14,199 kDa), nevertheless, in the lane that corresponds to the insoluble fraction. Yet, in the SDS-PAGE experiments for subunit hTrm9L, no bands were observed that could be attributed to this enzyme. We concluded that enzyme hTrm112 is satisfactorily expressed in self induction media and can be purified by means of affinity chromatography. Nevertheless, new tests must be accomplished to stabilize it in solution. Concerning hTrm9L, new cell transformation experiments must be accomplished. Once both proteins are satisfactorily produced, the next step is to solve their structure, either by x-ray crystallography or CryoEM.

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KEYWORDS: METHYLTRANFERASES, TRANSPORTER RNA, STRUCTURE DETERMINATION, PROTEIN EXPRESSION

POSTER PRESENTATION

FAST RIETVELD METHOD ALGORITHM FOR IN-SITU XRD

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X-ray diffraction is an analytical technique used to identify and quantify phases in a crystalline material. In a diffractometer, an X-ray with constant wavelength is directed to the sample which diffracts the wave in many directions with intensities that depend on the structure of the crystal. The result of the experiment is a diffractogram that presents the intensity of the diffracted wave at each measured angle. Each phase of the material results in a different pattern on the diffractogram, in such way that it is possible to quantify the amount of each phase in the sample. The Rietveld refinement method is probably the most used algorithm to refine the structure of crystals and to quantify the amount of each phase. The Rietveld method is based on the solution of a least-squares problem where it is minimized the difference between the diffractogram peaks collected in an experiment and a mathematical model of the crystal. Since the intensity of the peaks is proportional to the quantity of each phase in the sample, the method present good results in phase quantification. In-situ XRD comprises an experiment where many measures are made from the sample in different instances of time, resulting in a sequence of diffractograms that show the changes in the sample with time. It can be used to study and understand chemical reactions that form and consume different crystal in time. For instance, when cement is hydrated, many crystalline materials are consumed and formed until the reaction finishes. In many applications, in-situ XRD produces and huge amount of data, since samples may be collected once per minute for a complete day (or several days) resulting in thousand of diffractograms, where each one usually is close to one megabyte of data, totalizing gigabytes of data. This large amount of data is difficult to save and transport, but much more difficult is to analyze and to extract the information from each diffractogram, and to obtain useful information from these set of diffractograms. This problem is becoming much more relevant with the new sources of light like Sirius in CNPEM, since a brighter light allows shorter samples and therefore many more samples for each day. Rietveld refinement technique is usually performed by specialized people and requires a long time to extract the information of each sample, since many parameters need to be estimated resolving a non-convex optimization problem. Even experienced users may spend from tens of minutes to hours to resolve a single sample. In this work we present a new Matlab Toolbox used to quantify phases of a crystal using the Rietveld Refinement Technique specialized to In-Situ Samples. It is observed that since two consecutive samples present similar diffractograms then the estimated parameters of each sample should be similar, and then the optimal solution of one optimization problem is a good initialization parameter for the next one, resulting in faster time to resolve a sequence of diffractograms. The algorithm is implemented in Matlab and uses parallel programming capabilities to improve performance.

KEYWORDS: XRD, RIETEVELD, NUMERICAL METHOD

ORAL PRESENTATION

FORMATION OF NISI$_2$ NANOCRYSTALLINE PLATELETS ENDOTAXIALLY GROWTH IN SI(001) WAFER

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The interest in studies of $CoSi_2$, $TiSi_2$, NiSi and $NiSi_2$ nanocrystals integrated to the Si for application in nanointegrated devices has been increased in the last decades because these materials present high electrical conductivity, excellent thermal stability and are structurally compatible with the crystalline lattice of Si [1-2]. In this work an alternative method is proposed to obtain $NiSi_2$ nanoplatelets having the shape of regular hexagons embedded in single crystalline Si wafers. The method of preparation consist in the deposition of a Ni-doped thin film on a Si(001) wafer followed by thermal treatment to promote the diffusion of Ni throughout the SiO_2/Si interface and subsequent formation of the $NiSi_2$ nanoplatelets. The samples were characterized by X-ray reflectivity and grazing-incidence small-angle X-ray scattering. The results showed the $NiSi_2$ nanoplatelets grow coherently with crystalline lattice of Si having their hexagonal surface parallel to the lattice planes of the Si{111} crystallographic form and one of their lateral sides intercepting the wafer surface. The values of the lateral size and thickness of the nanohexagons determined from X-ray scattering analysis were L = (28.0 ± 0.6) nm and t = (3.0 ± 0.5) nm, respectively.

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KEYWORDS: NANOPARTICLES, NICKEL SILICIDE, GISAXS

POSTER PRESENTATION

GRAPHICAL USER INTERFACE DESIGN FOR X-RAY FLUORESCENCE TOMOGRAPHY DATA RECONSTRUCTION

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X-ray fluorescence tomography (XFCT) is a technique that allows reconstructing the 3D distribution of high-Z elements contained in a sample by measuring the x-ray fluorescence sinograms with photon-counting detectors. The technique can be used to analyze the distribution of elements in slices or volumes within different kinds of sample matrices in a non-destructive fashion [1][2]. In this work, the development of a new graphical user interface in Debian Linux for XFCT data reconstruction will be shown. It was written in Python3 and built in the way to be run through a Docker container [3]. The developed container runs all basic tools for accessing the C-library RAFT algorithms, used for XFCT image reconstruction [4] and the 3D visualization library VisPy. Its functioning and capability were tested by reconstructing the XFCT data collected from a seed of *Crambe abyssinica* plant [5]. The main improvement to speed up images reconstructions using a parallel and/or multi-threading programming approach is in progress. Regarding data collection at Carnaúba beamline in Sirius, complementary studies concerning the reconstruction of the global density of lighter elements from the scattered photons as well as the feasibility of image reconstruction for a limited number of projections, are underway.

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POSTER PRESENTATION

HIGH-RESOLUTION STRUCTURE OF A KAZAL-TYPE SERINE PROTEASE INHIBITOR FROM THE DENGUE VECTOR, *AEDES AEGYPTI*

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Haematophagic habits and urban habitat make the mosquito Aedes aegypti an important vector of a number of human viruses. Here, the high-resolution crystal structure of a non-canonical Kazal inhibitor from the saliva of Aedes aegypti, AaTI, is presented, providing a molecular explanation for its inhibitory profile. Blood-feeding exoparasites are rich sources of protease inhibitors and the dengue, yellow fever, Chikungunya, and Zika virus vector Aedes aegypti mosquito is no exception. AaTI is a single-domain, non-canonical Kazal-type serine proteinase inhibitor from Aedes aegypti that recognizes both digestive trypsin-like serine proteinases and the central protease in blood clotting, thrombin, albeit with three orders of magnitude lower affinity. Here we report the 1.4 Å crystal structure of AaTI, from extremely tightly packed crystals (~22% solvent content), revealing the structural determinants for the observed inhibitory profile of this molecule.

KEYWORDS: ANTICOAGULANTS, THROMBIN, TRYPSIN, SALIVARY GLANDS, KAZAL INHIBITOR, AEDES AEGYPTI, VIRUS

POSTER PRESENTATION

HIGH-VACUUM AND CRYO-COMPATIBLE DEVICE FOR APPLYING IN-SITU BI-AXIAL STRESS IN THIN-FILMS

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Thin films have a central importance in materials science and engineering and are extensively used in many fields of applied sciences. With the recent development of flexible electronics, and micro-electro-mechanical systems (MEMS) for applications such as electronic textiles, paperlike displays, roll-to-roll flexible solar cells, wearable or imperceptible sensors and high precision actuators, understanding how thin films react to mechanical stress, became even more relevant. This poster presents the development of a multipurpose biaxial mechanical stress rig designed for in-situ study of strained thin films by advanced synchrotron techniques. The device is capable to apply moderate loads (<400N) on two independent orthogonal axes with fine control of sample displacements and deformations. The control of both longitudinal and transversal stress components leads to a more accurate representation of the wide range of deformation which a film attached to compliant substrate may suffer. The instrumentation is adapted by construction to several experimental stations (beamlines) of LNLS and different sample environments (high-vacuum and low temperatures), allowing in-situ study of the effect of strain on thin films through x-ray diffraction, absorption, imaging and scattering advanced techniques. The instrumentation has been tested at XRD2 (diffraction) and PGM (soft x-ray absorption) beamlines of UVX source and will be fully available to SIRIUS users. A unique feature of the system developed is that one can keep the sample/substrate in a stretched condition at an independent low-profile transfer frame. By doing so, it is also possible to realize ex-situ measurements (like scanning probe microscopies) or making deposition (ex. sputtering) with the film/substrate already stretched. We present XRD stress analysis results for metallic and oxide thin-films grown by sputtering at cruciform shaped Kapton substrate, using a set of transfer frame and shadow mask which defines a 3 mm circular film. We take full benefit of the adapted design for diffraction, which features a completely free hemisphere above the sample to avoid shadowed areas, allowing the measurement of all three scattering components (Q_x, Q_y and Q_z). The evolution of lattice distortion for uniaxial, bi-axial and asymmetric loading paths reveals the elastic and plastic regimes for each path. For soft X-ray absorption measurements under cryogenic temperatures, a dedicated vacuum chamber has been developed. The details of the chamber, the cryogenic setup (cooper braid, cold-finger and mechanics), the geometry of total electron yield contacts and vacuum compatible mechanical assembly are presented in this poster.

KEYWORDS: THIN FILMS, STRESS, INSTRUMENTATION, XAS, XRD

POSTER PRESENTATION

HYDROGEN PRODUCTION BY THE THERMOCATALYTIC DECOMPOSITION OF METHANE USING A NICU/CMK-3 CATALYST

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Hydrogen has been gaining notoriety in recent decades since its burning is not aggressive to the environment and release even more energy than conventional fossil fuels. However, the productive process still releases large amounts of greenhouse gases, despite being cheap and possessing good yield. The process of Catalytic Decomposition of Methane consists of the direct breakdown of methane into solid carbon and hydrogen, in a moderately endothermic reaction. The hydrogen produced is high purity and the solid carbon produces very high nanocomposites commercial and scientific value. Without a catalyst, the process only occurs efficiently in very high temperatures, which makes it more expensive commercially, but the incessant efforts by the international scientific community are producing increasingly efficient catalysts, such as the nickel-copper system. CO_2-free production of hydrogen via thermocatalytic decomposition of methane in a microreactor was studied. The factors affecting NiCu catalyst supported in a CMK-3 mesoporous carbon is important both by the synergic effects due to the support. The effect of temperature on the H_2 yield was examined. Fibrous carbon nanotubes formed over Ni catalyst surface are of interest due to its commercial value. The hydrogen yield increased with increasing reactor temperature reaching 28% at 900°C.

KEYWORDS: HYDROGEN PRODUCTION, METHANE CONVERSION, HYDROGEN YIELD, CATALYTIC PYROLYSIS

POSTER PRESENTATION

IN-SITU CHARACTERIZATION OF STRAINED ANTIFERROMAGNETIC COO THIN FILM: A SYNCHROTRON RADIATION APPROACH

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The use of antiferromagnetic (AFM) thin films as active layers on spintronic devices brings new possibilities to this field's development. It happens, mainly, due to some interesting characteristics of these films, such as the existence of an ultrafast magnetization dynamics, an insensitivity to external magnetic fields and to the fact that they do not generate spurious fields. Although very promising, these features are also responsible for the greater difficulty of manipulating the spin orientation of AFMs when compared to ferromagnetic materials. One approach used for studying these materials is acting directly on its magnetocrystalline anisotropy (MCA) energy. This is done by making changes on the film's crystalline structure. This study aims to manipulate the spin axis orientation of an AFM thin film through the application of a controlled macroscopic strain. The film chosen for this study was Cobalt Oxide (CoO), grown using reactive magnetron sputtering technique. Bulk CoO is AFM bellow T=295K and has a strong MCA. For this work, a multi-purpose biaxial tensile device was used to apply strain onto a polycrystalline CoO thin film deposited on a stretchable cruciform Kapton substrate. This device allowed us to perform in-situ deformations on two orthogonal axes independently. Using X-ray stress analysis, we were able to use X-ray diffraction to study the deformation of the in-plane and out-of-plane film's lattice parameters. With this technique, we acquired information about the three components of the scattering vector, Q, by performing multiple theta-2theta scans for different ψ tilt angles. The deformation was then obtained by measuring the displacement of the sample's Bragg's peaks for the different strain states. Finally, to combine the data obtained using diffraction with the sample's magnetic behavior, an experiment of X-ray Magnetic Linear Dichroism (XMLD), using soft X-rays, was performed. XMLD is one of the few techniques sensitive to the magnetic ordering of AFM materials. In this technique, the probed intensity is proportional to both the expectation value of the square of the magnetic moment and the angle between the radiation polarization and the film's magnetic axis. Some preliminary XMLD results will be presented to complement the diffraction data.

KEYWORDS: SPINTRONICS, X-RAY STRESS ANALYSIS, X-RAY MAGNETIC LINEAR DICHROISM, ANTIFERROMAGNETISM

ORAL PRESENTATION

IN-SITU AND OPERANDO STUDY OF REACTION-INDUCED STRAIN ON MODEL CATALYSTS USING BRAGG CDI

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Gold nanoparticles are highly active catalysts for CO oxidation, although bulk gold is considered quite inert even to reactive molecules, the nanometer-size particles are efficient catalysts. Several effects contribute to the catalytic properties of supported nanoparticles catalysts such as particle size, morphology, exposed crystal facets, interaction with the support, low-coordinated atoms, strain effects and crystalline defects. During the reaction, nanoparticle surface goes under dynamic restructuration and expose different surface sites and defects with distinct reactivity. Understanding catalysts dynamic behaviours is crucial and requires the study of active sites IN-SITU and operando conditions. A peculiarity of CO oxidation reaction is the temperature hysteresis observed when during a complete cycle the catalytic properties do not match during heating and cooling. Explanations about the origin of this hysteresis loop are still conflicting. In order to investigate the facet-selectivity and dynamics involved in the active sites formation and the hysteresis behaviour we imaged the defects dynamics of gold nanocubes during CO oxidation reaction by Bragg CDI. Bragg CDI uses a coherent X-ray beam and phase-retrieval algorithms to image the 3D morphology of crystals and probe dynamic changes in strain and defects [1]. I will show how the anisotropic strain, occurring during the oxidation reaction, provides new understanding of the formation of the active sites in gold nanocrystals [2]. Significant changes were observed in the strain distribution during the reaction, regions of high tensile and compressed strain are concentrated on preferential facets in shape-controlled nanoparticles. The lattice strain can alter the reactivity of metal surfaces, strained metal surfaces have different chemical properties from those of unstrained surfaces due the shift in the d-band center. The tensile strain generation and release during the reaction directly influences the temperature hysteresis in CO oxidation. IN-SITU/operando strain imaging provide important insights to elucidate catalytic processes and designing catalysts with optimized morphology and defect control.

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KEYWORDS: BRAGG CDI, CATALYSIS, NANOPARTICLES

POSTER PRESENTATION

IN-SITU PHOTO SWITCHING OF SPIRORHODAMINES ISOMERS IN SOLID STATE: RATIONAL DESIGN OF PHOTOSENSITIVE MATERIALS

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At present, the functional materials structurally switchable by stimuli such as heat, addition of cations, changes of pH, pressure, or light are the motive of innumerable studies to be ideal models to investigate the relation structure-function and new properties derived from that change. In this work we studied a family of spirorhodamines (SRAs), which are photocromic molecules with a switching mechanism based on the differences in the fundamental electronic state between isomers in solid state photochemical reaction [1]. It involves changes in the molecule structure and is thermally reversible. In this work, assuming as hypothesis that in solid phase the permanence time in the optically active isomer in the range of the visible of a certain compound is associated with its structural characteristics, a family of compounds modifying the substituent were synthetized. These equilibriums were characterized in solid state by single crystal X-ray diffraction [2], atomic force microscopy coupled to infrared spectroscopy [2] and computational calculations, evaluating the changes produced after irradiating the corresponding close isomer with ultraviolet light for each compound.

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KEYWORDS: PHOTO SWITCHING, SPIRORHODAMINES, SOLID STATE, PHOTOSENSITIVE MATERIALS

Poster Presentation

IN-SITU STUDY OF THE PROCESS OF ADSORPTION/DESORPTION OF GASEOUS MOLECULES ON SUPPORTED ATOMIC QUANTUM CLUSTERS

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Atomic Quantum Clusters (AQC) are particles with well-defined structures and composition having a low number of atoms, below approximately 150 ($<\approx 1.7$ nm in size). The behavior of such clusters is different from nanoparticles of larger sizes because their sizes are comparable to the Fermi wavelength of the electrons (approx. 2 nm in Au, Ag or Cu). One of the main features of AQC is that the surface plasmon resonance – typical in metallic particles – disappears since all cluster electrons are covalently bonded [1]. Secondly, a band gap appears giving rise to semiconductor like (or molecular-like) properties, such as photoluminescence which is one of the most studied properties in metal clusters. This property of AQC makes them candidates for many applications, particularly in areas such as catalysis and photocatalysis[2]. In order to fabricate new efficient systems that can reach the industry and actual application, we need to test how these entities react with the environment, especially when supported on different substrates and exposed to different atmospheres, temperatures or external conditions, and study how these conditions can modify the AQCs electronic and physicochemical properties [3]. In this work, we performed a local structural characterization of Cu5 AQC clusters using X-ray Absorption Fine Structure Spectroscopy at the Cu-K edge in different conditions to understand their potential application for catalysis. In particular we characterized Cu5 AQC supported on different types of materials than can be interesting for the catalysis industry (Al_2O_3, SBA, TiO_2, ZrO_2, Graphite, etc.) in order to study their interaction with the different supports and determine how their electronic properties are modified by this interaction. Then, we studied the adsorption/desorption capacity of CO, O_2 and H_2 molecules at different temperatures on Cu5 supported on graphite, in order to use them as an active phase of catalysts for oxidation and hydrogenation reactions.

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Keywords: XANES, Cooper clusters, Catalysis, Adsortion, Desorption

POSTER PRESENTATION

IN-SITU SYNCHROTRON RADIATION EVALUATION OF HYDROGEN EMBRITTLEMENT IN ADDITIVELY MANUFACTURED STAINLESS STEEL

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The influence of hydrogen on the mechanical behavior and microstructure of 316 austenitic stainless steel (ASS) produced by direct metal laser sintering additively manufacturing technique was analyzed. For this, IN-SITU synchrotron radiation measurements of axial strain were made in both non-hydrogenated and hydrogenated specimens, using the X-ray Scattering and Thermo-Mechanical Simulation (XTMS), which is located at Brazilian Center for Research in Energy and Materials (CNPEM). X-ray powder diffraction (XRD) can be employed for phase identification in different crystalline materials, providing information on lattice parameters and dislocation densities. On one hand, hydrogen did not have a significant influence on the mechanical properties. Furthermore, a gain in ductility was observed under hydrogen effects. A similar behavior was observed in 304L ASS produced by additively manufacturing technique [1]. On the other hand, X-ray analysis evidenced the occurrence of phase transformations only under hydrogen effects. For hydrogenated specimen, the austenite (γ), which is a face-centered cubic lattice phase transformed into ε martensite, which is a hexagonal closest packed lattice phase. While for non-hydrogenated specimen, the martensitic transformation was not observed. Hence, in absence of hydrogen, the stress relaxation is related to the increase in the dislocation density of austenite. While under hydrogen effects, the stress relaxation is also related to strain-induced martensite. Hydrogen reduces the staking fault energy, favoring the formation of ε martensite. This increases the steel ductility. Contrary, hydrogen tends to reduce the ductility of commercial stainless steels since the austenite transforms into alpha martensite during strain (body-centered cubic lattice phase) [2,3]. This difference in the mechanical behavior is related to the characteristics of both martensites.

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KEYWORDS: AUSTENITIC STEEL, 3-D PRINTING, HYDROGEN

POSTER PRESENTATION

IN-SITU XPD AND XANES STUDIES ON $CE_{0.9}ZR_{0.1-X}SM_XO_{2-X/2}$ (X= 0.1, 0.08, 0.06, 0.04, 0.02, 0) IN DILUTED H_2 AND CH_4

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CeO_2-ZrO_2 mixed oxides are excellent electro-catalysts for oxidation reactions [1]. It was reported in previous works, that the oxide with composition $Ce_{0.9}Zr_{0.1}O_2$ is active as anode material for IT-SOFCs. Nevertheless, it is important to enhance its mixed conductivity (ionic-electronic) in reductive atmospheres [2]. In this sense, the substitution of Zr^{4+} by Sm^{3+} was proposed to incorporate vacancies in the oxide structure because of the different oxidation states of both cations, which in turn could have an impact on ionic conductivity. $Ce_{0.9}Zr_{0.1-x}Sm_xO_{2-x/2}$ (x= 0.1, 0.08, 0.06, 0.04, 0.02, 0) mixed oxides were synthesized via the citrate method. The aim of this work is to study the effective incorporation of samarium in the structure of the oxide and its stability by X-ray diffraction with synchrotron radiation in different atmospheres and temperatures. Besides, it is studied the effect of samarium incorporation on redox properties in diluted H_2 and CH_4 atmospheres (5vol.% in 50 mL.min^{-1}, He balance) from room temperature to 800°C and a heating rate of 10°C.min^{-1} by "IN-SITU" X-ray absorption spectroscopy (XAS) measurements performed at the Ce LIII absorption edge with synchrotron radiation. The evolution of Ce^{3+}/Ce^{4+} ratio with temperature in different atmospheres is studied. All samples showed the presence of a single phase corresponding to fluorite structure, characteristic of CeO_2, not only in air at room temperature but also, during thermal treatments with H_2 or CH_4. For samples calcined at 500°C average crystallite sizes are nanometric (< 10.3 nm) regardless the atmosphere. The increment in crystallite size and lattice parameter with samarium content is observed. Samples calcined at 1100 °C exhibit greater crystallite sizes but they are still nanometric. Experiments performed in diluted H_2 (5 vol.%) for samples calcined at 500 °C are in good agreement with traditional TPR. Two reduction steps are observed in the reduction profile of $Ce_{0.9}Zr_{0.1}O_2$, the first one corresponding to the reduction of superficial Ce^{4+}(ca. 550 °C) and the second one, at high temperatures (ca. 750 °C) related to bulk Ce^{4+} reduction [3]. The incorporation of Sm^{3+} substituting Zr^{4+} in the structure has a pronounced effect on the kinetics of reduction process and on the final degree of reduction. The two steps are still visible, but the final degree of reduction achieved is similar for all the samples tested. Samples calcined at 1100 °C show higher onset temperatures for Ce reduction. It is worth to mention that undoped sample, still presents two reduction steps while the others only show one indicating a surface loss with calcination temperature, compatible with the increment observed in average crystallite size. Experiments carried out with diluted CH_4 show similar results but it is worth to mention that lower total reduction values are obtained.

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KEYWORDS: CE-ZR-SM, NANOMATERIAL, XAS, XPD

POSTER PRESENTATION

IN-SITU X-RAY DIFFRACTION ANALYSIS OF THE IMPACT OF MICROSTRUCTURE ON THE AGEING BEHAVIOR OF TI-5553 ALLOY

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Ti-5Al-5Mo-5V-3Cr-0.5Fe (Ti-5553, composition in wt%) is a beta-metastable titanium alloy with improved strength and toughness properties over other beta-metastable alloys and is relatively easy to be processed, thus being highly competitive [1]. The high strength of beta-Ti alloys is due to the precipitation of fine laths of alpha phase within the beta matrix. These alloys lack nucleation sites for alpha, but form a metastable phase named omega. Omega is undesired in titanium alloys due to its embrittling effect. However, omega particles serve as nucleation sites for nanoscale alpha during ageing treatments [2]. The precipitation of alpha from omega may include the intermediate formation of another metastable phase, alpha" (alpha double-prime) [3]. The present study aimed to evaluate the effect of initial microstructural variation, given by thermal and thermomechanical treatments, on the ageing behavior of Ti-5553 alloy. The alloy was heat-treated and deformed by uniaxial compression at 950°C (beta phase field) and 800°C (alpha+beta field). Compression was carried out in a Gleeble(R) 3800 thermomechanical simulator with a strain rate of 0.001/s up to a compression ratio of 50%. Final microstructures comprised single beta grains with and without deformation-induced low-angle boundaries and a combination of beta and alpha phases in different proportions, depending on the processing route. Lattice defects, e.g. low-angle boundaries, may act as additional nucleation sites for phase precipitation [4], and the presence of alpha affects the composition of the beta matrix, which can also impact subsequent precipitation [5]. Ageing treatments were carried out at 400°C/8h with using x-ray diffraction in the XTMS experimental station of the XRD1 beamline of the Brazilian Synchrotron Laboratory. Results show that deformed conditions present higher initial amounts of omega after quenching in comparison with heat-treated conditions. In deformed conditions, XRD reflections of the beta phase have shown a sharp intensity decrease in the initial moments of ageing, which indicates an accelerated decomposition of this phase with respect to heat-treated conditions. In all conditions the precipitation of alpha" has taken place. In heat-treated conditions, the intermediate alpha" shows a stronger tendency to transform into alpha, whereas its evolution into the latter in deformed conditions is rather sluggish. In the condition heat-treated at 800°C, which presented a microstructure composed by a high amount of alpha phase prior to ageing (primary alpha), the precipitation of alpha" is hindered and the precipitation and coarsening of α is significantly enhanced, and therefore its hardness increase and final hardness are inferior to those from the other conditions.

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KEYWORDS: TITANIUM ALLOYS, THERMOMECHANICAL PROCESSING, AGEING, IN-SITU X-RAY DIFFRACTION

ORAL PRESENTATION

IN-VIVO X-RAY SPECTROSCOPY (XRF AND XANES) PROBING THE KINETICS OF ZNSO$_4$ AND ZN-EDTA ROOT-TO-SHOOT TRANSPORT ON SOYBEAN PLANTS (GLYCINE MAX)

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In the context of plant nutrition, zinc (Zn) is an essential micronutrient that plays a role in a range of vital processes, such as enzymatic activity and carbohydrate metabolism [1]. However, since around 50% of soils worldwide are Zn scarce [2], an external supply is required for the proper development of most crops. In this scenario, ZnSO$_4$, and chelated Zn-EDTA are two Zn sources commonly employed either for soil and foliar Zn supplementation [3]. In this study, we evaluated the root-to-shoot transport of ZnSO$_4$ and Zn-EDTA through soybean (Glycine max (L.) Merill) stems. For this purpose, the roots of soybean plants at the V4 growth stage were exposed to a hydroponic solution containing ZnSO$_4$ and Zn-EDTA at 100 mg Zn L^{-1}, respectively. The stems were in vivo monitored along 48h using a handheld X-ray fluorescence spectrometer (XRF, Bruker, Tracer III SD, USA) for Zn uptake kinetics and then, by X-ray absorption near edge structure (XANES) spectrometry on the XAFS2 beamline of the Brazilian Synchrotron Light Laboratory (LNLS) for the Zn chemical speciation evaluation. At the end of the experiment, chemical µ-XRF (Orbis PC, EDAX, USA) maps of fresh stem tissues transversely cut and Zn quantification on root and leaves tissues were also performed. We observed that Zn content in the stems of the plants exposed to ZnSO$_4$(aq) was around 10-fold higher when compared with that with Zn-EDTA(aq) and above 50-fold higher than in the control plants. The Zn uptake presented an exponential increasing followed by a drop. Although present a similar uptake velocity for both treatments, the point at which the uptake rate starts decreasing was achieved faster for Zn-EDTA(aq) (9.4±1.3 h) than for ZnSO$_4$(aq) (29.5±1.7 h), showing that soybean plants were able to control the uptake of Zn-EDTA(aq) earlier than ZnSO4(aq), resulting in the higher Zn content found in the plants exposed to ZnSO$_4$(aq). In the other hand, XANES spectra allow stating zinc is biotransformed in its way up to the shoot as different forms of zinc, regardless of exposing source. Since the XRF chemical maps show that Zn is found simultaneously in transport tissues (i.e xylem and phloem), as well cortex tissues, it is feasible to assume that it could be at different chemical species in each of these environments.

KEYWORDS: XRF, XANES, CHEMICAL SPECIATION, IN VIVO, SOYBEAN

ORAL PRESENTATION

INDUCED MAGNETIZATION AT INTERFACIAL CU ATOMS IN EPITAXIAL FE/CO/CU3AU(001)

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Induced magnetization has already been observed in some non-magnetic metals, as Pd, Rh or Pt, due to proximity effect with ferromagnetic films. For Fe or Co ultrathin films grown on Rh(111) substrate, the Rh atoms show a significant induced magnetic polarization, as determined by X-ray magnetic circular dichroism (XMCD) measurements at Rh M2,3 edges. Pd, Rh, and Pt are close to satisfying the Stoner criterion for magnetism [2], and a ferromagnetic order is expected for ultrathin films [1]. On the other hand, Cu has a Stoner parameter of only 0.08, far away from the unit value required to fulfill the Stoner criterion, and is not expected to be magnetic [2]. However, induced magnetic moment in Cu atoms has been previously observed in Cu spacers in systems like Fe/Cu, Co/Cu or Co/Cu/Pt multilayers [3,4]. In this work, we investigate the induced magnetism in Cu at the interface between alternate Fe/Co monolayer films and a Cu3Au(001) substrate. The Cu3Au(001) was prepared by sputtering (1500 eV) and annealing (850 K) cycles. Fe/Co samples were prepared by alternate evaporation of Fe and Co monoatomic layers (5 ML). The films were grown and characterized at the PGM beamline at the Brazilian Synchrotron Light Laboratory (LNLS). The structure and epitaxy were monitored by LEED and RHEED. XMCD measurements at Cu, Co and Fe L2,3 edges at 30 K and 300 K were performed. Clear magnetic dichroism has been observed on Cu atoms in this system. We have shown that the induced magnetization is larger at lower temperatures and that, when the monolayer in contact with the substrate interface is Fe, the induced moments are larger than when the interface monolayer is Co. First principle calculation is needed to better understand the induced moments and the proximity effect mechanism in this system.

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KEYWORDS: INDUCED MOMENTS, PROXIMITY EFFECT, XMCD

POSTER PRESENTATION

INELASTIC HARD X-RAY SCATTERING SPECTROSCOPY: RESULTS AT UVX/LNLS AND PROPOSALS FOR SIRIUS

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Since the advent of high-brightness radiation sources in the range of hard X-rays, spectroscopic studies based on the inelastic scattering of X-rays have gained a growing interest due to the feasibility of performing experiments with high energy resolution and a high photon flux. A general breakthrough in this technique was driven by high brilliance undulators inserted at high-energy third-generation synchrotrons, providing new experimental possibilities. Inelastic X-ray scattering (IXS) spectroscopy comprises multiple regimes, which are able to provide fundamental information about the electron system in the condensed matter, as excitation dynamic of a many-electron system, structure of unoccupied electronic states, core-hole interactions or ground state properties of the scattering electron system [1]. Additionally, the use of a high penetrating probe (hard X-rays) allows that true bulk information can be obtained and that samples in special environments can be investigated. This way, IXS has become a well established technique in the last years, having been implemented in dedicated beamlines at several synchrotron radiation laboratories around the world. Inelastic X-ray scattering has been also applied to a broad range of analytical studies, among others, high pressure studies of materials of interest in geophysics [2], IN-SITU studies of processes and materials for energy applications [3] or spectroscopic tomography with sensitivity to light elements and chemical contrast [4]. Our work performed in the field of IXS at UVX/LNLS in the last years [5-7] will be summarized, new IXS experiments that could be carried out at SIRIUS will be discussed and new related instrumentation, in particular X-ray analyzers for IXS will be proposed.

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KEYWORDS: X-RAY SPECTROSCOPY, INELASTIC X-RAY SCATTERING, ELECTRON EXCITATIONS

POSTER PRESENTATION

INFLUENCE OF EU VALENCE IN THE BATIO$_3$ DECORATED WITH CAF$_2$ SYNTHESIZED BY MICROWAVE-ASSISTED HYDROTHERMAL METHOD

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Systems with doping and double layer are examples of the promising materials for application in photoanodes of the DSSC cells [1-2]. Unlike the other works that involve the interaction of materials, we consider obtaining a photoanode promoting a single step of deposition of the material. Therefore, in this work, we developed a system containing Barium Titanate ($BaTiO_3$) decorated with Calcium Fluoride (CaF_2) undoped and doped with Europium. We performed the synthesis of these systems by the hydrothermal method assisted by microwave. Besides the advantage of obtaining the system with shorter times and low temperatures of synthesis, it is also possible to ensure the control of the composition of both phases in the system. For comparison, we also performed the synthesis of the CaF_2 doped with Eu. In both the undoped and doped system, X-ray diffraction (XRD) patterns indicated the formation of two phases, belonging to the $BaTiO_3$ core and the CaF_2 decoration. Transmission electron microscopy images show differences between the systems and the isolated compounds. The X-ray Absorption Near-edge Structure (XANES) on the LIII edge of Eu, for the samples: $BaTiO_3$ with CaF_2:Eu and CaF_2:Eu showed predominance of the Eu^{3+} species (Absorption edge in 6980 eV). However, for the sample containing only CaF_2:Eu, a small shoulder (6974 eV) can be visualized related to the presence of Eu^{2+}. This result is in line with the behavior of the excitation and UV-Vis-IR emission spectra of the samples around LIII edge of Eu. The measurements of emission and excitation in the range of 5.6-15 eV were performed in the TGM beamline. The emission spectra showed bands of associated to the transitions of the Eu^{2+} and Eu^{3+}. It is possible to visualize that the intensity of these transitions reversed as the excitation energy varied. The exciton formation is identified and is due to the emission band around 200-300 nm. The difference in the optical behavior of the samples may indicate that Eu3+ ions are also in the matrix and/or surface of the $BaTiO_3$. Thus, the method of synthesis can have incorporated the ions of Europium in the two compounds.

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KEYWORDS: EUROPIUM, HYDROTHERMAL MICROWAVE, LUMINESCENCE, DSSC

Poster Presentation

IN-SITU DXAS STUDY OF NIO/CEO$_2$-SM$_2$O$_3$ NANOCOMPOSITES FOR IT-SOFC ANODES UNDER REDUCING AND PARTIAL OXIDATION OF METHANE CONDITIONS

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Fuel cells are promising devices for environmentally clean energy production by directly converting chemical energy into electricity. Among them, solid-oxide fuel cells (SOFCs) have the unique capability to use different fuels such as hydrocarbons or H_2. However, several issues have to be solved in order to improve their efficiency and reduce their costs. The reduction of their working temperature, which is typically around 900-1000°C, is one of the most important issues. For this reason, extensive research has been devoted to develop novel materials for intermediate-temperature SOFCs (IT-SOFCs). CeO_2-based anodes have proven to exhibit excellent catalytic properties. Besides, these materials are mixed ionic/electronic conductors (MIECs) under reducing atmosphere and, therefore, fuel oxidation can take place on its entire surface, while it only occurs in the [anode/electrolyte/gas] interphase (triple-phase boundaries) for electronic conductors. In recent works, we investigated the performance of nanostructured CeO_2-based anodes for IT-SOFCs [1]. Nanomaterials are not employed in conventional SOFCs since grain growth is expected to occur at high temperature, but their use in IT-SOFCs is currently under evaluation. Anodes based on nanostructured MIECs are very interesting because the number of active sites for fuel oxidation is expected to increase dramatically. The aim of this work is to take further insight into the catalytic properties of Ni/CeO_2-Sm_2O_3 composite under reducing and partial oxidation of methane (POM) reaction condition [1-3]. Dispersive X-ray absorption spectroscopy (DXAS) technique was used in the Ce LIII and Ni K absorption edges in order to determine the oxidation states of cerium and nickel cations in the reaction conditions prevailing in the catalytic studies. The influence of the sample morphology was evaluated by analyzing samples subjected to different thermal treatments, finding that the samples calcined at lower temperatures had a higher reducibility in both the Ni and Ce and the reduction process is completed at a lower temperature. However, all the studied materials exhibit similar performance under partial oxidation of methane conditions.

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Keywords: Ni/CeO$_2$-Sm2O3, IT-SOFCs, Anode, Methane partial oxidation

POSTER PRESENTATION

IN-SITU SAXS AND XAFS STUDY OF ULTRATHIN GOLD NANOWIRES FIRST STAGES OF FORMATION

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Ultrathin gold nanowires (AuNW) have attracted great interest due to their unique conductivity properties making them suitable candidates for a myriad of applications. Many relatively simple synthesis protocols have been reported using gold salts and surfactants, in general $HAuCl_4.3H_2O$ and oleylamine (OAm), resulting in micrometer long wires with sub 5 nm diameters [1] [2]. In order to gain control over the final product of the synthesis it is necessary to understand the different stages involved in the process, characterizing in detail the structures generated along the way. In a recent report, we proposed a several stage process for the formation of AuNW at room temperature in hexane studying the oxidation state and atomic coordination of gold by X-ray absorption fine structure (XAFS) spectroscopies at Au L3 edge, and the shape and sizes of the nanostructures by small angle X-ray scattering (SAXS) [3]. However, the reaction velocity at room temperature does not allow a proper determination of the gold atomic environment in the early stages of the synthesis, especially the Au coordination with Cl and OAm. Moreover, it is still not clear how Au-OAm complexes form, through aurophilic interactions, the discs precursors of the nanowires. Herein we present an Au L3-edge EXAFS spectroscopy study (XAFS2 beamline at LNLS, Campinas, Brazil) performed at low temperature (~6 K) in order to decrease the reaction velocity and determine how Au coordination changes in the first moments of the synthesis from Au^{+3} in the gold salt, coordinated with Cl atoms, to Au^{+1} in the Au-OAm complex, coordinated with N atoms. In addition, Cl K-edge XANES spectroscopy experiments were performed at SXS beamline (LNLS, Campinas, Brazil) to clarify how Cl coordination evolves during the synthesis and in-situ small angle X-ray scattering experiments were performed at SAXS1 beamline (LNLS, Campinas, Brazil), with 60 s temporal resolution, to study how Au-OAm complexes interact and give rise to the initial structures that generate the AuNW.

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KEYWORDS: GOLD NANOWIRES, XAFS, SAXS

ORAL PRESENTATION

INTERACTION OF AG AND ZN NANOPARTICLES IN THE SEED COAT OF COMMON PHASEOLUS VULGARIS DURING THE GERMINATION INVESTIGATED BY SYNCHROTRON-BASED TECHNIQUES

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The presence of nanoparticles (NP) in agricultural inputs is a clear fact, as can be seen in many patents involving this application [1]. The nano form can improve the performance of these, but may also bring risks to the environment since the fate of nanomaterials is poorly understood. This application of nanotechnologies can result in more rational use of pesticides, biocides, and fertilizers [2]. Seed treatment is an extensive practice to provide micronutrients. The treatment of the bean seed coat before the sowing can be performed in a safer way compared to the common dispersion method in the field. My PhD. project investigates the effect of ZnO and Ag NP on the germination of seeds of Phaseolus vulgaris and the mechanism of interaction in the seed coat. Were propose ZnO and Ag NPs as a seed treatment, to improve the seedling growth providing micronutrients and protection to the crop. The common bean seeds treatments and synchrotron analysis were performed at the ID21 beamline in ESRF, CENA-USP and XRF beamline in LNLS. The bean testa presents three different layers, which are objects of this study. The seeds were exposed to Ag_2S, Ag metallic, ZnO NP, $AgNO_3$ and $ZnSO_4$ in different concentrations (Ag 100 and 1000 mg L^{-1} while Zn 100, 1000 and 5000 mg L^{-1}). After 5 days of post-treatment and germination, seed coats were recovered and sectioned to FTIR measurements and in cryo conditions to µ-XRF maps and µ-XANES. From µ-XRF analysis provides the localization of Ag and Zn in the different seed coat tissues, µ-XANES spectra show changes in the chemical environment for each treatment and FTIR provides information about changes in the regions of the mid-IR spectrum i.e. carbohydrates, proteins, and lipids induced by these treatments. The combination of these results can contribute to building another step in the understanding of how nanoparticles can improve agricultural inputs and benefit food crops.

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KEYWORDS: X-RAY ABSORPTION SPECTROSCOPY; X-RAY FLUORESCENCE, SYNCHROTRON-BASED FOURIER TRANSFORM INFRARED, COMMON BEAN SEED COAT

POSTER PRESENTATION

INVESTIGATION OF OSSIFICATION IN *T. MILIARIS* TADPOLE

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A great enigma of modern biology is how the geometry of muscular and skeletal structures are created and how their development is controlled during growth [1]. X-ray microcomputed tomography have become, in particular for amphibians, to be used as an important tool in biological research, by virtue of it is non-invasive method allowing to carry out more accurate studies on the morphology of anuran, such as skeleton, muscle, ocular structure and leaves the specimen intact [2]. In this work, synchrotron X-ray computed microtomography and phase contrast has been exploited for a qualitative and quantitative analysis of ossification in the Thoropa miliaris tissues. The collected specimens are stored in Herpetology Laboratory at Biological Science and Healthy Institute (Rural Federal University of Rio de Janeiro). The micro-CT measurements were carried out in IMX beamline at Brazilian Synchrotron Light Laboratory (LNLS) White or pink beam (filtered with silicon) were used to scan sample. Images were acquired with 5x or 2x magnification lenses, which gives a virtual pixel size of 4.11 µm and 1.64 µm. Depending of sample size we used 1000 projections over 180° or 2000 projections over 360°. The distance sample-to-detector was 20 cm to increase phase contrast effect. Herein we describe a formation of endolymphatic calcium deposits (ECD) and bone at different stages of growth of the Thoropa miliaris specimens.

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KEYWORDS: SYNCHROTRON, MICROTOMOGRAPHY, BIOLOGY

POSTER PRESENTATION

IRON OXIDES PREPARED FROM STEEL WASTE FOR APPLICATION TO ADSORPTION

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Iron oxides are found in natural or synthetic form and can stabilize in different crystalline structures depending on the chemical reactions involved. They can be synthesized through different physical or chemical methodologies [1] and a possibility is the acid digestion of ferrous metal compounds [2]. This methodology can be used to mitigate environmental problems by the recycling of metallic waste, such as steel. Steel, as a metal material of great demand, can be recycled without losing its properties or being transformed in new iron compounds. These compounds can be applied as adsorbents to remove harmful substances from water used in textile process and thus creating a cycle to control contaminants through materials previously called pollutants. In this work, two iron oxides were synthesized, LClNH and TClNH, from stainless steel and carbon steel, respectively, through acid digestion with HCl (1 mol L^{-1}) and precipitation with NH_4OH (5 mol L^{-1}), to application as adsorbent of organic congo red. Data about structure, composition and materials properties were obtained through X-ray fluorescence (XRF), X-ray diffraction (XRD), X-ray absorption near edge structure (XANES), zeta potential and analysis BET. The elementary composition corresponds to ferrous metallic precursors, which means the material produced from stainless steel presents Cr in its composition, along with Fe, different from TCINH. The diffractograms presents peaks of higher intensity at angles of 21° and 36°, corresponding to the mixture from goethite and magnetite formation (ICSD: code #184786 and #250540), to both the materials. The results of XANES corroborate the XRD ones, and the spectrum, when compared to the patterns, have the profile of Fe^{+3} and Fe^{+2} mixture. Synthesized oxides were promissing as adsorbents. Literature reports that iron compounds applied as adsorbents to congo red have a quantity of adsorbat adsorbed by adsorbent of 200 mg g^{-1}, in general [3], and in this work values of 480 mg g^{-1} to LCINH and 151 mg g^{-1} to TClNH, in environmental temperature. The oxides efficiency of adsorption is justified because the dye used is anionic and zeta potential results were high positive, of 40 mV (LCINH) and 43 mV (TClNH), contributing to adsorption process. Since zeta potentials does not have significant differences, BET technique showed that the material possessing higher adsorption has superficial area of about two and a half times the TCINH area, which explains the inequality of adsorptive capacity between them.

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KEYWORDS: ADSORPTION, IRON OXIDE, WASTE

POSTER PRESENTATION

LOCAL STRUCTURAL STUDY OF $\mathrm{BATI_{1/2}MN_{1/2}O3}$ DISORDERED DOUBLE PEROVSKITE BY EXAFS SPECTROSCOPY

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$\mathrm{BaTi_{1/2}Mn_{1/2}O_3}$ (BTMO) is a 12R-type perovskite where the M(2) transition metal site is occupied by Mn/Ti while M(1) and M(3) sites are occupied by Mn and Ti, respectively. Such scenario permits the formation of trimmers, dimmers and the presence of Mn orphan spins [1]. Dc-susceptibility measurements reveal no magnetic order down to 2 K [2], what make BTMO a candidate to exhibit quantum spin-liquid behavior [3]. The emergence of this state of matter is intimately related to the distribution of spins in the crystal, and so to the M(2) site occupation. In this work we present local-structural study of BTMO by EXAFS spectroscopy at Mn K edge at 12, 150 and 300 K to investigate the atomic neighboring distribution of Mn at M(1) and M(2) sites.

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KEYWORDS: MAGNETISM, X-RAY, SPECTROSCOPY

ORAL PRESENTATION

MAGNETO-ELASTIC COUPLING IN FEPT/BATIO$_3$ STRUCTURES

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The design and fabrication of multiferroics is one of the main challenges for the development of oxide spintronics. Tuning the magnetic state by electric field or strains appears to be the key for low-energy devices. Magneto-electric and magneto-elastic coupling at interfaces between ferromagnetic and ferroelectric layers are at the origin of these phenomena [1]. First-principle calculations revealed recently that important changes of magnetic anisotropy should be observed on FePt/BaTiO$_3$ structures when BaTiO$_3$ is poled [2]. Moreover, BaTiO$_3$ piezoelectric and FePt magnetostrictive properties make FePt/BaTiO$_3$ heterostructures a highly tunable multiferroic. To study magneto-elastic coupling in the FePt/BaTiO$_3$ structures, we grew by sputtering a series of these bilayers onto (001) SrTiO3 substrates. The crystalline structure of the bilayers was extensively characterized by X-ray diffraction experiments performed at the XRD2 beamline of the Laboratório Nacional de Luz Síncrotron – Campinas while magnetometry, magnetic force microscopy and micromagnetic simulations were the experimental techniques used to investigate the magnetic behaviour of FePt/ BaTiO$_3$ system. In this work we present an analysis of our experimental results and the correlation found between strains induced by SrTiO$_3$ substrates, the BaTiO$_3$ thermal expansion coefficient and the FePt magnetic properties. Our results allow us to get a deep insight into the magneto-elastic coupling mechanism through FePt/BaTiO$_3$ interfaces.

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KEYWORDS: MAGNETOELASTIC, MULTIFERROIC, THIN FILMS

POSTER PRESENTATION

MECHANICAL ALLOYED NI$_{60}$S$_{40}$ NANOCRYSTALS STUDIED UNDER HIGH TEMPERATURE AND HIGH PRESSURE CONDITIONS

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Metal sulfide nanomaterials have attracted great interest in the scientific community due to their excellent performance in energy storage applications and, recently they have been employed in supercapacitors [1]. Ni_3S_2 is a metal sulfide that occurs naturally as the mineral heazlewoodite and synthesized by different methods [2-4]. Li *et al.* [5] presented the synthesis of Ni_3S_2 nanoparticles via a mechanical alloying method combined with a post heat treatment that exhibits a high specific capacitance of 911 F g^{-1} at 0.5 A g^{-1}. Here we report, a simple one-step mechanochemical synthesis of Ni_3S_2 nanocrystalline powders. Ni_3S_2, was prepared mechanochemically using ball milling in an inert atmosphere at room temperature, starting from $Ni_{60}S_{40}$ powder mixtures. X-ray powder diffraction (XRPD) was used to investigate the structural and microstructural evolution of the $Ni_{60}S_{40}$ alloy with milling time. The formation of trigonal Ni_3S_2 phase (space group R32H) occurs with only 1.5 h, remaining stable up to 24 h of milling. The cell volume, lattice parameters, atomic coordinates and isotropic atomic dislocation (thermal) parameters of the Ni_3S_2 phase, as well as its average crystallite size and micro-strain, were determined from Rietveld analysis of the XRPD data. The average crystallite size decreases from about 37 nm to 22 nm with milling time increasing. The micro-strain also decreases with milling time increasing. The high-temperature experiments showed that the melting point of the nanocrystalline Ni_3S_2 is about 660 °C, which is much lower than bulk. Transmission electron microscopy (TEM) images and electron diffraction patterns confirmed the nanometric size of the crystalline domains but revealed that it belongs to larger agglomerated particles (~100 nm). The nanocrystalline samples have their magnetic properties characterized by vibrating sample magnetometer (VSM), showing an evolution from ferromagnetism to a mixed magnetic state as milling time increases. The high-pressure experiments revealed no phase transitions up to 20 GPa and a bulk modulus of about 143 GPa for the Ni_3S_2 nanophase using the least-squares fit of first-order Murnaghan equation of states.

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KEYWORDS: NANOCRYSTALLINE NI3S2, HIGH-TEMPERATURE, HIGH-PRESSURE

POSTER PRESENTATION

(MICRO)STRUCTURAL CHARACTERIZATION OF W-DOPED CACU$_3$TI$_4$O$_{12}$ CERAMICS

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$CaCu_3Ti_4O_{12}$ (CCTO) based ceramics has been widely investigated due to its wide range applicability that is a result of it multifunctional properties, such as dielectric [1], non-ohmic [2], gas sensing [3] photoluminescent [4] and photocatalytic [5]. Extensive (micro)structural characterization was carried out on CCTO / x % W6+ powders. The ceramic powders were prepared using the solid state reaction method. X-ray diffraction (XRD) was performed to investigate the long-range order of the material. All samples show a single CCTO phase, which has a cubic perovskite structure and space group Im3¯(ICSD card 32-002). The Rietveld method was used to calculate the crystalline and unit cell parameters and compare the samples among them and the literature. The experimental data were successfully fitted using the Split Pseudo-Voigt (SPV) function, and the Rietveld values (Rp, Rwp, Rexp, Rbragg and χ2) indicate an effective refinement in accordance to the literature. Short-range order was characterized using Raman spectroscopy. Five Raman modes were identified experimentally (192, 270, 434, 544 and 597 cm-1). The geometry and oxidizing state of Ti ions was studied through X-ray absorption near edge structure (XANES) around the Ti K-edge. The peaks identified on the pre-edge region are associated to the octahedral coordination of the Ti^{4+} ions on each of the samples [6]. All samples present pre-edge features A, B and C associated to the transition of excited 1s electrons into the bands t2g and eg of the octahedral field. Scanning electron microscopy (SEM) was performed to determine the morphology and particle size on the powders. All samples exhibit a single-mode particle size distribution over a relatively narrow range indicating homogeneity of the powders. The Kubelka-Munk method was used to obtain a relation between absorbance and the band gap energy from the UV-visible spectroscopy data. This work is a preliminary (micro)structural investigation of CCTO/W6+ ceramic powders aiming at photoluminescent and photocatalytic applications.

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KEYWORDS: CACU3TI4O12, HR-XRD, RAMAN, XANES

POSTER PRESENTATION

MICRO-CT AND X-RAY DIFFRACTION: AN ONTOGENY INVESTIGATION OF *T. MILIARIS* TADPOLE

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Micro-CT has been used as an important tool in biological research, in particular for amphibians, due to its is non-invasive method allowing to carry out more accurate studies on the morphology of frogs, such as skeleton, muscle, ocular structure and leaves the specimen intact [1]. A peculiar species of tadpole called *Thoropa miliaris* [2], found along the Brazilian Atlantic Rain Forest, reproduces under extreme environmental conditions and lives in water films that run along rock outcrops along the forest, near or isolated from river and rivulets [3]. In early stages post-hatching of the egg [4], *T. miliaris* tadpole presents deposits of calcium carbonate crystals in their lymphatic glands, known as endolymphatic calcium deposits (ECD), which are composed of aragonite and likely represent an important source of calcium for bone formation during and after metamorphosis [5]. *T. miliaris* tadpoles were scanned in the X-ray microtomography beamline (IMX) at Brazilian Synchrotron Light Laboratory (LNLS) to obtaining a detailed anatomical description of soft tissue. Images were acquired with 5x or 2x magnification lenses, which give a virtual pixel size of 4.11 µm and 1.64 µm. Depending of sample size we used 1000 projections over 180° or 2000 projections over 360°. The distance sample-to-detector was 20 cm to increase phase contrast effect. Tomographic images were obtained with and without silicon filter depending on the type of sample (different stages of development, ECD or extracted bones) and the exposure time that it was submitted to optimize image quality. Specimen of *T. miliaris* has tissues whose densities are similar and IMX beamline afforded to obtain tomographic images, improving excellent edge definition between regions of different tissues. Furthermore, by means of X-ray diffraction (XRD1 beamline, with energy of 12 keV) we evaluated different stages (from 25 to 46) of the specimen *T. miliaris* in order to verify the mineral composition of the remaining samples, such as crystal structure of the ECD and bones. The new Brazilian synchrotron light source, Sirius, will allow us to carry out quantitative and qualitative analyzes with higher quality and fast acquisition time for biological interest (i.e., morphology, ontology, heterochrony), as well as development of new methodologies for biological samples.

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KEYWORDS: SYNCHROTRON, MICROTOMOGRAPHY, X-RAY DIFFRACTION, BIOLOGY

POSTER PRESENTATION

MICRO-CT PHANTOM CALIBRATION IN SYNCHROTRON LIGHT SOURCE USING MICROSTRUCTURED OPTICAL FIBERS

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Micro-CT technique is a largely used tool for three-dimensional material characterization. The application of this technique can be used in different research areas as, for example, biomedical science [1], biology [2], geology [3]. Within this context, the development of a proper characterization protocol designed for the quantification of not only the resolution but also the observed gray scales would be of great value. However, the spatial resolution available at today's micro-CT is beyond what a typical machine desktop would achieve preventing the manufacturing of a reliable phantom. On top of that, there is also the need to choose not only the density of the phantom but mostly the need to calibrate the amount of any given element within the phantom[4]. Finally, for the case of a multipurpose micro-CT, both the resolution requirement and the elemental specificity would need to be prompt adjusted following the needs of any given sample. In this work, we used microstructured optical fibers with diameter of 125 micron as sample holders for spatial and density calibration. The fiber containing one or more holes, with diameter of about 25 micron was filled with Na_2CO_3, $CaCl_2$, $CaCO_2$ solubilized in water (solutions ranging 0.9M to 3.6M) to create standard in order to study the capability (in micro-CT experiment) to differentiate similar densities. The scans were carried out in IMX beamline at LNLS (Campinas-SP, Brazil). For each scan 1000 projections were taken over 180°, the beam was filtered using 200um Si and total scan time was about 30 min.

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KEYWORDS: MICRO-CT, OPTICAL FIBERS, X-RAYS, NONLINEAR OPTICS

Oral Presentation

MICROMECHANICAL ASPECTS OF THE AUSTENITE REVERSION IN A HIGH-MN STEEL EVALUATED BY IN-SITU SYNCHROTRON X-RAY DIFFRACTION

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High-Mn steels are very attractive for automotive applications, since they combine high strength and ductility [1]. The transformation-induced plasticity (TRIP) is one of the complex strain hardening mechanisms presented by these steels. With regard to the TRIP effect, metastable austenite (gamma) transforms into epsilon- and/or alpha'-martensite. Reversion annealings of Mn-based steels transforms the alpha'-martensite back to austenite, leading to remarkable bulk-scale grain refinement [2]. In this work the austenite reversion in a 17.6 wt.%Mn steel was tracked by means of in-situ X-ray diffraction (XRD). This experiment was carried out at the X-Ray Diffraction and Thermo-Mechanical Simulation (XTMS) workstation placed at the LNNano. The material was deformed to an engineering strain of 0.2 under tensile testing and further annealed up to 800°C with a heating rate of 3°C/min. During in-situ experiments, images of the diffraction cones were collected under a rate of 6 pictures per minute. The 2D images were converted into usual diffractograms which were fitted with a pseudo-Voigt function to obtain the integrated area, peak position, and the full width at half maximum (FWHM) of the peaks. The phase quantification was performed using the direct comparison method [3]. The modified Williamson-Hall approach [3] was used to separate the contributions from the crystallite size (D) and lattice strain (beta) to the peak broadening. The starting and finishing temperatures for the epsilon -gamma reaction was 245 and 450°C, respectively. The corresponding temperatures for the alpha'- gamma transformation were 450 and 700°C, respectively. From the beta behavior, it was observed that tempering occurs in the alpha'-martensite in the early stages of the gamma reversion. The crystallite size in turn increases considerably in the end of this reaction. In addition, the changes in the molar volume of the steel was assessed from the lattice parameters of the phases.

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Keywords: In-situ XRD synchroton, Austenite reversion, 17.6wt.%Mn steel

POSTER PRESENTATION

MICROSTRUCTURAL CHARACTERIZATION OF NITE$_2$ NANOCRYSTALS BY WIDE ANGLE X-RAY TOTAL SCATTERING (WAXTS)

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Here we present a structural and microstructural characterization of $NiTe_2$ nanocrystals (NCs) performed using conventional XRPD data from the LDRX/UFSC and WAXTS measurements from the XRD1 beamline [1] of the Brazilian Light Source (UVX – LNLS). We will present a comparison between conventional methods of data analysis (notably the Rietveld method [2]) and the total scattering method (considering Bragg peaks and the diffuse scattering caused by the sample) using the models based on the Debye Function Analysis (DFA) [3, 4]. For that, we have used Rietveld-based program packages (TOPAS [5] and GSAS II [6]) and DebUsSy [7] program package developed by one of our collaborators, Dr. Guagliardi. A critical discussion will be done considering the two main advantages of the DFA approach, compared to conventional Rietveld-based methods: i) Bragg and diffuse scattering are treated on an equal basis (meaning that the whole experimentally available information is used), and ii) grounded on atomistic models of NPs, structure, defects, finite size and morphology can be simultaneously considered. Similarly to the Rietveld method, the DFA approach [4] enables the calculation of the total scattering pattern of randomly oriented NPs that can be directly compared to (and adjusted against) the experimental data. In addition, unlike the PDF analysis [8], the DFA does not transform the experimental data, thus keeping the advantage of simultaneously dealing with both reciprocal and direct spaces. We will also highlight in this presentation that although the DFA approach do not need to use high energy photons to reach large Q-range data, since, differently from PDF, the fitting of the patterns generated from atomistic models is doing in the direct space and not in the reciprocal one, when dealing with high absorbing elements it could mandatory to have high energy photons to overcome issues related with data reduction. We intend to show how the transmitted beam from the filled capillary must be independently measured in order to estimate the sample absorption coefficient, while the computed X-ray attenuation factors from the nominal glass composition must be used for the empty capillary. Further issues on the angle-dependent intensity corrections (including inelastic Compton scattering signal) applied to the raw data, using routines developed at Swiss Light Source (SLS) [9], will be also presented.

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KEYWORDS: NICKEL DITELLURIDE (NITE2), WIDE ANGLE X-RAY TOTAL SCATTERING (WAXTS), RIETVELD

ORAL PRESENTATION

MODIFIER CATIONS IN SILICATE GLASSES - POSSIBLE CHANGES OF THE LOCAL STRUCTURES DURING THE VERY EARLY STAGES OF CRYSTALLIZATION

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Crystallization is a key issue in understanding glass formation and plays a fundamental role in the development of advanced glass-ceramics. In the absence of catalyzing agents, most supercooled liquids crystallize heterogeneously from the external surfaces; only a few systems crystallize homogeneously in the interior. To gain further insight into the nucleation mechanism and the role of nucleating agents, it is essential to follow the formation of the first nuclei. An open issue about the early stages of nuclei formation in glasses is the following: which structural changes occur, especially in the local order around the network modifier cations (Na, Ca, Mg, Ba, etc.) and potential nucleating agents (Fe, Ti, Zr, etc.), during the pre-crystallization stage? (when a glass is heat-treated for several hours at copious nucleation temperatures, but before significant crystallization takes place). Is the whole local structure around the cations modified well before crystallization is completed? The precise role of nucleating agents in glass-ceramic formation will likely only be understood by investigating the very first stages of crystallization with a strictly local structural probe having atomic selectivity. The X-ray Absorption Fine Structure (XAFS) technique is quite appropriate to characterize the local structure of specific cations present in glassy samples from the earliest stage of crystal nucleation. In this work, partially crystallized and fully crystallized samples were obtained after treatment at temperatures and times defined in previous studies. The XANES and EXAFS spectra of selected cations ions in the BaO-SiO_2, $Ba_2TiSi_2O_7$, $CaMgSi_2O_6$ – 9 mol% Fe_2O_3, MgO-SiO_2, 1NaO-2CaO-3SiO_2 and 2NaO-1CaO-3SiO_2 glassy systems were collected at room temperature by using the transmission and total electron yield modes. A preliminary analysis of the data indeed showed modifications in the local order around some cations as the time of crystallization increased. The results will be fully discussed.

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KEYWORDS: SILICATE GLASSES, CRYSTALLIZATION, LOCAL ORDER, XAFS

ORAL PRESENTATION

MODULATING THE ASSEMBLY OF MAGNETIC NANOPARTICLES BY THEIR SURFACE MODIFICATION WITH DIFFERENT POLYMERS

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Magnetic nanoparticles are very versatile platforms for producing materials for a wide range of applications. Their intrinsic magnetic property can be explored to drive the material to a specific target, to concentrate or phase separate, to guide its assembly, to produce local heat, etc. [1]. In addition, the nanoparticles functionalization by grafting polymers to the surface is a promising strategy to promote the colloidal stability, to include additional functionalities and also to tune their interfacial properties, inducing the assembly to interfaces or into hierarchical structures. Depending on the chemical characteristics and responsivity of the attached compounds, these interactions can be modulated selectively by the solvent composition or different environmental stimuli, as temperature, pH, ionic strength and electromagnetic radiation, leading to interesting possibilities as smart materials [2]. In this project we used the grafting-to approach for the surface modification of maghemite nanoparticles (y-Fe_2O_3) using phosphonic acid-terminated polymers in order to modulate their interfacial properties and self-assembly. We explored the grafting of a mixture of two chemically distinct polymers (PEO and PMMA) to induce amphiphilicity and perhaps, surface anisotropy through their segregation into patchy or Janus domains. The presence of a binary coating was demonstrated by spectroscopic techniques (FTIR and XPS) and thermogravimetry (TGA) and the nanoparticles assembly was investigated by scattering techniques (DLS and SAXS). The assembly extension could be adjusted by varying the polymers ratio during preparation and also by varying the solvent composition. The known co-solvency behavior of PMMA in ethanol aqueous solutions also showed to affect the colloidal stability of the particles and can be used to modulate the assembly. Moreover, the modified particles showed to be interfacial active, being able to stabilize oil-in-water pickering emulsions that respond to an external magnetic field. In a second approach, we explored the inclusion of an additional property by preparing maghemite nanoparticles grafted with a thermoresponsive polymer (poly-N-n-propylacrylamide, PNnPAm). We found that the thermoresponsivity of the coated particles could be enhanced or inhibited depending on the pH and ionic strength of the dispersion, due to residual free phosphonic acid groups. We demonstrate that imposing two orthogonal stimuli such as magnetic field and temperature and adjusting the pH and ionic strength, we can trigger the alignment and assembly of the nanoparticles forming micrometer-size flexible filaments with magnetic-responsive properties. In summary, the surface modification of iron oxide nanoparticles using phosphonic acid-terminated polymers has shown to be a very versatile strategy to improve the applicability of magnetic nanoparticles, to tune its interfacial properties and to induce oriented assembly forming magnetically-active hierarchical structures.

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KEYWORDS: MAGNETIC NANOPARTICLES, ASSEMBLY, INTERFACIAL PROPERTIES

POSTER PRESENTATION

MOLECULAR ORIENTATION AND CHARGE TRANSFER DYNAMICS OF MODIFIED GO:PEDOT:PSS COMPOSITES FOR OPTOELETRONIC APLICATIONS

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Organic Solar Cells (OSC) are photovoltaic devices that convert solar radiation into electric current. In these systems, the anode usually consists of glass or plastic covered by a thin layer of transparent conductive oxide, such as indium tin oxide (ITO), acting as a hole transport layer. The cathode is made of low work function metals, such as aluminum that acts as electron transport layer. The photoactive layer consists of donor materials (p-type semiconductor polymers) and electron acceptors (such as fullerene derivatives). The most common OSCs can be constructed in bi-layer or bulk heterojunction architectures, which differ in the way the donor and acceptor units are distributed along the photoactive layer. One aspect that causes concern in the architecture of the current OSCs is the ITO anode, which presents some disadvantages (mainly for being expensive and easy to break when deflected), resulting in an unwanted setting of device upscaling. Therefore, the substitution of this material is of great relevance for the continuity of the research and production of the OSCs. The conducting polymer poly(3,4-ethylenedioxythiophene)–polystyrenesulfonic acid (PEDOT:PSS) is certainly one of the most important substitute material reported for indium tin oxide in organic devices. Although graphene oxide (GO) is not a good conductor, it can form high-quality thin films and can be transparent, and additionally, GO is an inexpensive material and can be easily synthesized. PEDOT: PSS blended with GO films were evaluated by X-ray photoabsorption (NEXAFS) for molecular orientation studies and Resonant Auger Electron Spectroscopy (RAS) using the Core-Hole-Clock method (CHC) for charge transfer dynamics investigations. The opposite behavior of the pi* and sigma* transitions in the NEXAFS spectra suggests that the thiophene-unit in PEDOT is preferably oriented with the molecular plane perpendicular to the substrate surface. Furthermore, no clear angular dependence was observed for PSS, which indicates that the sulfur units of this polymeric dopant film have a more amorphous nature. The charge transfer times showed a decrease from about 5 fs for GO:PEDOT:PSS 5% to 4.3 fs for the GO:PEDOT:PSS 5% treated in ethylene glycol nanocomposite. These spectroscopic results suggest that the simple solvent treatment using ethylene glycol proved to be efficient and able to increase the conductivity of the nanocomposite films.

KEYWORDS: ORGANIC SOLAR CELLS, NEXAFS, RAS

POSTER PRESENTATION

MOLECULAR ORIENTATION AND CHARGE TRANSFER DYNAMICS OF TERPOLYMER FILMS FOR OPTOELECTRONIC APPLICATIONS

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The integration of donor-acceptor (D-A) functional units has been widely used as a strategy for designing more efficient copolymers to optoelectronic devices [1]. In the present work, four terpolymers – three statistical and one block – films composed by 9,9-dioctylfluorene (A), 2,1,3-benzothiadiazole (B) and 9-(9-heptadecanyl)-9H-carbazole (C) monomers in addition to two others terpolymers – one statistical and one block – composed by A and C along with 4,7-dithien-2-yl-2,1,3-benzothiadiazole (D) monomer were evaluated by X-ray photoabsorption (NEXAFS) and resonant Auger electron (RAES) spectroscopies. According to transitions intensities variation with the incident angle of the photon beam at the S K-edge photoabsorption spectra, all films present a well-defined molecular orientation in which all the units with a sulphur atom in the copolymer has a preferred "lie down" geometry. By employing the core-hole clock (CHC) method [2] from RAES results, ultrafast charge transfer times were estimated for each film. The polymers with the D monomer showed a low charge transfer time for most of their resonances while the ones with B monomer yield longer times, possibly reflecting the acceptor character of this unit [1].

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KEYWORDS: SEMICONDUCTING POLYMERS, X-RAY PHOTOABSORPTION SPECTROSCOPY, RESONANT AURGER ELECTRON SPECTROSCOPY, CHARGE TRANSFER TIME

ORAL PRESENTATION

NEW APPROACHES FOR MICROSTRUCTURAL CHARACTERIZATION OF NANOCRYSTALLINE POWDERS BY WIDE ANGLE X-RAY TOTAL SCATTERING (WAXTS)

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In this presentation I intend to show how the concept of total scattering (considering Bragg peaks and the diffuse scattering caused by the sample) using the models based on the Debye Function [1] can improve the characterization of the nanocrystalline powders. The innovative part in the characterization of the microstructure proposed consists in using advanced synchrotron Wide Angle X-ray Total Scattering (WAXTS) techniques and the Debye Function Analysis (DFA) available in DebUsSy [2] program package developed by one of our collaborators, Dr. Guagliardi. For many nanocrystalline materials XRPD is mainly used as a qualitative tool to correctly gauge the presence of a given crystalline phase. Conventional methods of analysis of XRPD data (notably the Rietveld method [3]) fail to consider important information contained in diffuse scattering, typically observed in disordered and/or nanometric materials [1, 4]. Due to the co-presence of multiple sources of peak broadening and aiming at performing the size and strain analysis on data free of instrumental broadening, the best to do is to resort to synchrotron WAXTS measurements and advanced modeling techniques based on the DFA [5]. When dealing with NPs, the DFA approach has two main advantages, compared to conventional Rietveld-based methods: i) Bragg and diffuse scattering are treated on an equal basis (meaning that the whole experimentally available information is used), and ii) grounded on atomistic models of NPs, structure, defects, finite size and morphology can be simultaneously considered. Similarly to the Rietveld method, the DFA approach [6] enables the calculation of the total scattering pattern of randomly oriented NPs that can be directly compared to (and adjusted against) the experimental data. Recently, we have presented a thorough structural and microstructural characterization of Fe_5Te_4 NPs [8], performed using WAXTS measurements from the X04SA-MS beamline [7] of the Swiss Light Source. We have presented an innovative microstructural model, integrating the effects of microstrain within the DFA modeling of a population of spherical NPs of variable size. We provided a quantitative estimate of the defectiveness (microstrain) of this nanosized material. A newly developed protocol for microstrain analysis, integrated with structure, size and morphology information, indicates the presence of highly strained nanoparticles, with strain preferentially accumulated in the ab-plane than along the c-axis of the tetragonal structure. I'm totally convinced that similar innovative structural and microstructural characterizations using WAXTS measurements can be performed in the new Brazilian synchrotron (Sirius).

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KEYWORDS: NANOCRYSTALS, WIDE ANGLE X-RAY TOTAL SCATTERING (WAXTS), DEBYE FUNCTION ANALYSIS (DFA)

POSTER PRESENTATION

PREPARATION AND STRUCTURAL CHARACTERIZATION OF NANOSTRUCTURED MULTIFUNCTIONAL CO-DOPED ZNO:MN:ZR OXIDE

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ZnO is a well-known multifunctional material. Its applicability spans over a broad spectrum of scientific and technological areas, going from photocatalysis, optoelectronics, biomedical applications, spintronics, etc. Concerning its magnetic properties once doped with transitional metal (TM) elements, the so pursuit ferromagnetic behavior, in spite of the great effort in the last two decades, is still one of the most challenge issue in the materials science and condensed matter physics. Here, the consensus is that the simple doping with TM is not a sufficient condition to achieve the ferromagnetism in such systems, and that punctual defects like zinc interstitial (Zni) and vacancies (VZn) plays an important role into get the task. In this work we show the studies about the preparation and the structural characterization of a multifunctional oxide based on the ZnO doped with Mn and co-doped with Zr ($Zn_{1-x-y}Mn_xZr_yO$). The objective of the Zr-dopping is due, once Zr^{+4} is substituting the Zn^{+2} in the ZnO structure, via charge compensation process, we can introduce vacancies in the Zn sites in a controllable way. The samples were prepared via the method of polymeric precursors in the nominal concentrations of xN = 0.03 (3 at.%) and yN = 0.005, 0.010, 0.015 and 0.020 (0.5, 1.0, 1.5 and 2.0 at.%). The structural characterization was performed via X-ray diffraction analysis, Raman scattering spectroscopy, X-ray absorption spectroscopy. The results show a partial incorporation of the dopants into the wurtzite ZnO structure with some unknown secondary phases.

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KEYWORDS: MULTIFUNCTIONAL, FERROMAGNETISM, STRUCTURAL DEFECTS, STRUCTURAL CHARACTERIZATION

POSTER PRESENTATION

PROTECTIVE EFFECT OF LOSARTAN IN ARTERIES OF RATS SUBMITTED TO RADIOTHERAPY FOR BREAST CANCER

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Breast cancer (BC) survival is increased by the diagnosis of earlier-stage disease and treatments improve, however, the side effects of cancer treatments, such as cardiotoxicity, remain clinically important. Radiotherapy for breast cancer often involves some incidental exposure of the heart to ionizing radiation. Women with breast cancer who are treated with adjuvant radiation have a decreased risk of local recurrence but an increased risk of mortality from coronary artery disease (CAD). The possible reason to occurrence of CAD after radiotherapy is the unfavourable remodelling of the coronary artery due the radiation injury. Although the effects of cardiotoxicity induced by BC treatment are well known, its precise mechanisms are not completely elucidated. Losartan is an angiotensin II type 1 receptor (AT1) antagonist widely used for the treatment of hypertension as well as other cardiovascular diseases. Previous studies showed the efficacy of losartan to correct the altered structure and endothelial dysfunction of resistance arteries from patients with essential hypertension, and also prevent the progression of coronary atherosclerosis in patients with significant atherosclerotic disease. The present study aims to clarify how the radiotherapy for breast cancer affects the coronary artery and to determine if losartan can be used to minimize the side effects of the irradiation in this artery. Determination of the distribution and chemical state of elemental constituents within biological systems at sub-cellular level down to trace level concentrations is of growing importance for gaining new insights about the highly complex functions of elements within the tissue or cells. CARNAÚBA (Coherent X-Ray Nanoprobe Beamline) is the tender-to-hard X-ray nanoprobe under construction at the new Brazilian synchrotron light source SIRIUS. The beamline provides two separated experimental stations, one with sub-micrometer resolution and another with nanometer resolution, to cover various analysis techniques, including X-ray fluorescence (XRF). The all achromatic CARNAÚBA optics will covers continuously the energy range from 2 to 15 keV. With this energy range, it will be possible to analyze K-lines of light elements, like phosphorus and sulfur, and also heavier elements, like calcium and zinc. The use of CARNAÚBA beamline will provide both submicrometer spatial resolution and elemental mapping of important elements in coronary artery of hypertensive rats allowing analyze the tissue in a cellular level.

KEYWORDS: CORONARY ARTERY, XRF, RADIOTHERAPY

POSTER PRESENTATION

RADIATION DAMAGE IN BIOLOGICAL SAMPLES PRODUCED BY SYNCHROTRON MICRO-CT

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X-ray microtomography (micro-CT) is applicable over a wide range of size scales encountered in biology. As a noninvasive method, micro-CT imaging can produce finely resolved images of internal morphology of biological samples in their natural state and without elaborate and time-consuming dissection or histology, showing high efficiency, high precision, and wide potential applications of synchrotron X-ray phase-contrast micro-CT [1, 2]. The combination of microtomographic techniques as well as the exceptional properties of third-generation synchrotron radiation sources allows obtaining volumetric information of a specimen at micron or sub-micron scale with minimal sample preparation. These advances are now being extrapolated to make the fourth-generation machines become reality, such as Sirius at the Brazilian Synchrotron Light Laboratory (LNLS) [3]. Unfortunately, radiation damage is an inherent and unavoidable part of any imaging experiment using ionizing radiation (IR). IR is known to form different kinds of radicals in the sample. Whereas for pure water the radical species are very well known, much less is known about the X-ray induced radical species in biological samples. The advent of new diffraction-limited storage rings which will produce even brighter synchrotron beams further stresses the necessity of increasing our knowledge of the X-ray radiation damage issue [4, 5]. In our previous study in this area [6], radiation damage was induced through X-ray microscopy (XRM) measurements carried out at the TwinMic soft X-ray microscopy beamline at Elettra synchrotron Facility [7] to detect structural changes and Fourier transform infrared microspectroscopy (FTIRM) to detect possible chemical changes. Further experiments of this type to correlate radiation-dependent effects on the sample chemistry and the tissue morphology (for instance, micrometric cracks, holes or uniform mass loss) would be useful. This abstract builds on our previous work [6] moving from paraffin-embedded biological tissues to investigating the effect of X-ray induced damage on whole biological specimens during micro-CT analysis. Radiation damage resulting from the high absorbed doses needed in micro-CT imaging of organic materials often limits both achievable contrast and spatial resolution. Recently, we applied micro-CT to study tadpoles [8] in order to describe external and internal morphological features like cartilage, muscles, sacs containing calcium, crystalline, and skin at a range of developmental stages. The micro-CT images were obtained at the imaging beamline (IMX) at LNLS. The specific purpose of the present work is to investigate chemical (through FTIRM) and morphological (through micro-CT) changes induced on tadpoles samples at exposure conditions commonly employed at MOGNO beamline at Sirius.

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KEYWORDS: MICRO-CT, PHASE-CONTRAST, RADIATION DAMAGE, BIOLOGICAL SAMPLES

POSTER PRESENTATION

RECENT XRD AND XSW INSTRUMENTATION DEVELOPMENT ADDRESSING FUTURE SAGUI BEAMLINE APPLICATIONS

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Up to now, the XRD2 is one of the UVX beamlines in charge to perform scattering and diffraction experiments, especially those ones that take advantage of either its 6-circles Huber diffractometer or its vast options of different experimental setups, ranging from GISAXS (Grazing-Incidence Small-Angle X-Ray Scattering) to HR-XRD (High-Resolution X-Ray Diffraction [1]). With SIRIUS being ready in the short-term, some instrumentation is currently under development for the SAGUI – Scattering Analysis Beamline, which is being designed to allow high-speed data acquisition of three-dimensional Reciprocal Space Maps (3D-RSM) and also add elemental sensitivity to XRD via X-ray Standing Wave (XSW) technique [2]. Under XRD measurements, the incident and diffracted waves undergo interference and cause the XSW both inside and near the crystal surface. When probing an element, one can observe a change (modulation) on its fluorescence signal and then infer about its position in the crystal lattice. Therefore, XSW combines the elemental sensitivity from X-ray Fluorescence (XRF) with the spatial resolution from XRD, which is useful for studies of alloys or doped-crystals when distinguishing atomic sites supply essential information to understand macroscopic effects, such as superconducting [3], thermoelectric [4], or magnetic alloys [5], and in Crystal Engineering [6]. Recently, XSW was successfully performed at XDS beamline on GaAs and S_2O_6-doped $NaBrO_3$ crystals, firstly aiming commissioning the experimental setup, and then to discriminate between interstitial or substitutional incorporation of the S (Sulphur) atom into the $NaBrO_3$ lattice, respectively. Regarding the RSM, obtaining a reciprocal space volume around a reciprocal lattice point (RLP) is seen as the natural evolution from the usual approach, where the diffracted intensity is shown in a 2D contour map in terms of out-of-plane and in-plane directions. Therefore, the 3D-RSM delivers intensity distribution all over the reciprocal space coordinates providing information on the averaged morphology [7], strain [8], and lattice relaxation at the interface region between adjacent domains [9]. Allying the high-intensity increase from XRD2 to SAGUI and a fast area-detector, 3D-RSM is expected to support in-situ studies under applied external fields, as well as temperature-dependent dynamics [10]. Here, results from both XSW and 3D-RSM techniques performed using UVX beamlines will be shown and discussed regarding the setup, data processing, and technological improvements currently planned for the SAGUI beamline.

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KEYWORDS: X-RAY DIFFRACTION, X-RAY STANDING WAVE, RECIPROCAL SPACE MAP, SAGUI

POSTER PRESENTATION

REDOX PROPERTIES AND CATALYTIC PERFORMANCE FOR METHANE OXIDATION OF NIO/CE$_{(1-X)}$M$_{(X)}$O$_{(2-D)}$ (M = GD, SM, Y, ZR) NANOCOMPOSITES: IN-SITU DXAS STUDIES

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CeO_2-based materials have received great attention due to their excellent catalytic properties for oxidation reactions. The incorporation of a metal oxide in the CeO_2 lattice can modify the oxygen storage capacity, ionic conductivity and specific surface area of these catalysts, so a wide variety of materials and applications are currently under investigation. In the field of new anodic materials for IT-SOFCs, CeO_2-based anodes are subject of intense study because they have proven to exhibit excellent performance, not only in hydrogen-fueled SOFCs, but also operating with hydrocarbons. These excellent properties of CeO_2-based anodes are probably related to the fact that they are mixed ionic/electronic conductors (MIECs) under reducing atmosphere and, therefore, fuel oxidation can take place on its entire surface, while it only occurs in the [anode/electrolyte/gas] interface (triple-phase boundaries) for electronic conductors. It is important to point out that the number of active points for fuel oxidation are dramatically increased in nanostructured, high specific surface area MIECs. In this work, we will compare the redox properties and the catalytic performance for methane oxidation of several CeO_2-based nanopowders and NiO/CeO_2-based nanocomposites, treated at different temperatures in order to get materials with different average crystallite sizes. We performed dispersive X-ray absorption spectroscopy (DXAS) studies at the D06B-DXAS beamline of the Brazilian Synchrotron Light Laboratory (LNLS, Brazil) on ZrO_2, Gd_2O_3, Sm_2O_3 or Y_2O_3-doped CeO_2 nanopowders (ZDC, GDC, SDC and YDC, respectively) and also NiO/ZDC, NiO/GDC, NiO/SDC and NiO/YDC nanocomposites under different atmospheres and reaction conditions. We found that CeO_2-based materials with small average crystallite size and high specific surface area exhibit the best redox properties, while the catalytic performance for methane oxidation depends on the dopant used in the CeO_2-based phase.

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KEYWORDS: CeO_2-BASED CATALYSTS, IT-SOFCS, DXAS

POSTER PRESENTATION

RESONANT SYNCHROTRON X-RAY DIFFRACTION AS IMPORTANT TOOL TO IDENTIFIED CRYSTALLINE PHASES IN PARTICULATE MATTER

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Recent publications have studied particulate matter (PM) present in air [1,2]. This subject has been investigated in the last decades due to its association with respiratory and cardiovascular health problems, due to the potential to penetrate the innermost alveolar region of the lungs and the bloodstream. Some evidence suggests the association between the PM chemical composition with biological response, including the role of transition metals, such as iron (Fe), and their potential for oxidative stress in cells and production of reactive oxygen species. Taken into account, the crystalline phase characterization of PM is imperative to identify compounds with such characteristics providing subsidies for air quality management. Particle Matter samples were collected at two sampling sites in the Region of Greater Vitória, Espírito Santo, southeast of Brazil. As considering a previous elemental analysis, performed by X-ray Fluorescence, it was done a crystalline phase investigation performed by Resonant Synchrotron X-ray Diffraction at Laboratório Nacional de Luz Synchrotron in Campinas, Brazil. The results showed uncommon species not reported in the literature in PM, that were associated with the proposed mechanism of reactions suggested specific sources as responsible for that crystal, acting as specific source markers. $BaTiO_3$ was found in PM samples and showed could be associated to vehicular marker formed during break actions. Other same uncommon crystal phases were found in PM, maghemite (γ-Fe_2O_3), ammonium perchlorate (NH_3OHClO_4) and potassium ferrate ($K_2Fe_2O_4$). Each one showed could be associated with a specific mechanism of formation, in which links those crystalline phases to specific sources, such as sintering, pelletizing and coke making. This study reveals that Resonant Synchrotron X-ray Diffraction is an important tool to identify these components. In addition, this works shows that this technique helping researchers to infer the main sources contributing for the deterioration of air quality, even without the use of receptor models.

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KEYWORDS: CRYSTALLINE PHASES, RESONANT SYNCHROTRON X-RAY DIFFRACTION, SOURCE MARKERS, PARTICULATE MATTER, UNCOMMON SPECIES

POSTER PRESENTATION

RETRIEVING THE CONFIGURATION OF INTERFACE STRUCTURE IN HEXAGONALLY CLOSE-PACKED MATERIALS BY SYNCHROTRON X-RAY FORBIDDEN REFLECTION ANALYSIS

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Despite all progress in improving desirable properties in metallic materials through alloying, mechanical processing and thermal treatments, knowledge of the interface structure down to nanoscale is crucial for designing materials with new regimes of property-performance space. The interface structure of polycrystalline metallic materials (such as grain boundaries, subgrain boundaries, twin and twist transition boundaries) can strongly influence their properties. Despite the large body of work, there are still important questions on interfaces of metallic systems that remain unanswered, particularly regarding their atomic arrangements [1]. These arrangements have been mainly characterized by imaging techniques such as scanning and transmission electron microscopy (SEM/TEM), which can access structural data locally, but are destructive and statistically limited. Methods that rely on large-area results which are statistically relevant, such as X-ray diffraction (XRD), may lack of a direct interpretation or depend of specific modeling. Recently, the continuous development of third generation synchrotron sources and diffractometer systems with broad-range detectors has opened the possibility of analyzing extremely weak X-ray reflections through the acquisition of a complete diffractogram with excellent reciprocal space resolution and very large count rate, offering higher accuracy and signal-to-noise ratios. In this work, a Mythen 24K detector covering up 120° of scattering angle was used to accumulate counts from synchrotron XRD experiments on commercially pure Mg samples. An acquisition time of 1 h allowed the retrieval of preferential interface structure configurations through the observation of very weak diffraction peaks. Additional peaks were located close to the Mg (102), (200), (204) and (300) fundamental reflections. A kinematical simulation [2] scanning possible interface structures was performed to establish the correspondence of non-bulk peaks with the interfacial structural organization of atoms which may be responsible for such scatterings. The simulated interfaces were probed for a wide range of angular displacements with respect to the main cleavage planes of the bulk system; as the angles and inclusion interfaces are varied, we are able to retrieve the configurations that produce diffraction peaks with appreciable intensity at positions that were compatible with the additional peaks observed experimentally. The information about the maximum strain at the interface plane (with respect to a pure bulk configuration) and their geometry may be related with conditions that lead to local energy minimization [3] with a symmetry that allows for XRD, representing a long-range ordered pattern of atomic distributions in Mg. The introduced methodology allows for monitoring changes in a system when it undergoes mechanical processes that refine grain sizes and modify grain orientation, for instance. The inherent characteristics of X-rays drives this methodology beyond the microscopy surface analysis, providing at the same time statistical relevance and depth capabilities, thus rendering such approach unique in the field of Materials Science and Engineering.

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KEYWORDS: X-RAY DIFFRACTION, SYNCHROTRON, INTERFACES, FORBIDDEN REFLECTIONS

POSTER PRESENTATION

SAXS APPLIED TO THE STUDY OF THERMOSENSITIVE LIPID PLATFORMS FOR CONTROLLED DRUG DELIVERY

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Drug Delivery Systems (DDS) is a promising area of nanomedicine that has been actively developed to maximize the therapeutic effects of drugs. The efficiency of DDS performance depends on the system used. In this sense, liposomes are very attractive systems, as they naturally have several desirable characteristics to act as DDS, such as biocompatibility, biodegradability, stability in biological fluids, having different chemical environments in their structure and not being immunogenic. Although self-organizing in aqueous medium, lipid-formed structures can be controlled and fabricated according to the purpose of the application. However, this spontaneous organization is not efficient in terms of preparation time, system homogeneity, material utilization and reproducibility of physicochemical characteristics. Microfluidics, which is microscale fluid engineering, emerges as a technology that can overcome most of these challenges. In this doctoral project the microfluidic technique is being used to produce thermosensitive liposomes with potential to act as DDS, with controlled structural (shape, size, polydispersity and lamellarity) and controlled physical-chemical (colloidal stability, transition temperature) properties. For the characterization of the produced systems were used the techniques of DLS (Dynamic Light Scattering), Zeta potential, DSC (Differential Scanning Calorimetry) and SAXS (Small-Angle X-ray Scattering). Using the phospholipids DMPC (1,2-dimyristoyl-sn-glycero-3-phosphocholine), DMPG-Na (1,2-dimyristoyl-sn-glycero-3-phospho- (1'rac-glycerol) (sodium salt) and mDSPE-PEG (1,2-distearoyl-sn-glycero-3-phosphatidylethanolamine-N-[methoxy (polyethylene glycol) -2000] from the SAXS technique it was possible to observe the unilamellar profile of the structures formed by a one step method, changes in structure through the evaluation of the electron density profile of the bilayer upon temperature variation, showing its thermosensitive character. From the other techniques it was observed that the systems are nanometric (<100 nm), have low size dispersion, stability for 7 days, without aggregation and without large variations in surface potential, demonstrating that the method used is efficient for producing good DDS candidates.

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KEYWORDS: LIPOSOMES, MICROFLUIDIC, SAXS, DRUG DELIVERY SYSTEM

POSTER PRESENTATION

SEASONAL FE AND MN SPECIATION IN ATMOSPHERIC PARTICULATE MATTER FROM PIRACICABA AND ITAPETININGA CITIES (SP) BY X-RAY ABSORPTION SPECTROSCOPY

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Characterization of atmospheric particulate matter is mandatory in order to identify and quantify polluting compounds, as well as to elucidate its origin and hazard potential [1]. In this scenario, synchrotron-based X-ray spectroscopy techniques, and, specifically the X-ray absorption near edge structure (XANES), are important tools to study the chemical environment of elements present in particulate matter. Fe is considered a significant source of reactive oxygen species (ROS), harmful compounds to human health [2]. In addition, it is reported as the most abundant transition metal in aerosols. Mn is also a relevant metal for monitoring in the particulate matter. This latter metal may be originated from diesel-burning vehicles [3]. The present study aimed at determining the chemical speciation of Fe and Mn in coarse particulate matter (particle size between 2.5 and 10 µm known as PM10) collected in Piracicaba (industrial city having ca. 400 thousand habitants)and Itapetininga (mostly agricultural city having ca. 150 thousand habitants) municipalities during the summer and winter seasons of 2018. The PM10 samples were collected during 60 hours, using a time-sequenced particulate sampler (Streaker, PIXE International, USA), with PM10 sequentially sampled in each 6 h. XANES spectra at Mn and Fe K edges were recorded using a ca. 500 x 100 μm^2 focused beam in fluorescence geometry at XAFS2 beamline of the Brazilian Synchrotron Light Laboratory (LNLS). A set of Fe and Mn salts were as referential standards. The results suggest that Mn is presented as Mn^{3+} and Mn^{2+}, XANES features are similar to those of Mn_2O_3, $MnPO_4$, and $MnSO_4$ standards. In addition, Fe is presented as Fe^{3+} mostly as hematite form. The suspend soil particles are the likely source of Mn and Fe in the collected particulate.

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KEYWORDS: ATMOSPHERIC PARTICULATE MATTER, PIRACICABA AND ITAPETININGA CITIES, FE AND MN SPECIATION

ORAL PRESENTATION

SHEDDING LIGHT ON LIGHT GENERATING MATERIALS: XEOL, EXAFS, XANES, PHOTO AND THERMOLUMINESCENCE AND TIME RESOLVED EXPERIMENTS “TOOLBOX” REVEALING THE DYNAMICS OF CHARGED CARRIERS

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Spectroscopy techniques associated to UV, vacuum ultraviolet (VUV), X-rays beams available in synchrotron sources are very useful tools for a variety of scientific problems in a broad range of areas from biomolecules, soft matters up to very hard materials. In material science spectroscopy techniques targets basically the electronic states and, depending on the energy of the photons of the excitation beam and the rate of energetic deposition in the material, various dynamic processes are triggered, from localized electronic excitation to large area and long extended and multielectronic-multiphonic processes. In the present work the application of such techniques is surveyed for a group of materials of interest to radiation detection and luminescent pigments aiming the identification of the key processes related to the applications, as follows: 1- Nd-doped Y_2O_3 nanoparticles, useful material for a variety of applications in radiation detection and also in luminescence thermometers; 2- Ba based fluorides, like BaY_2F_8 BaF_2, high effective Z hosts with wide X-ray absorption and featuring interesting luminescence characteristics, like intrinsic luminescence and core-valence luminescence; 3- LiLaPO:Ce that exhibits one of the fastest time response scintillation with high yield; 4- $CdWO_4$, a high efficient blue emitter scintillator that has been tested as scintillator screen for the micro and nanotomography Sirius beamline, and 5- $CaYAl_3O_7$, pure and doped, new material with fast response and intrinsic luminescence. All systems were synthesised in our laboratory under controlled conditions and structurally characterized. EXAFS, XANES, XEOL, VUV spectroscopy and time resolved XEOL and luminescence were investigated using all facilities installed in the XAFS2, SXS and TGM beamline of the UVX storage ring at LNLS. In parallel, models of the dynamics of the generated charged carriers were devised for each of the system and the relevant features for the applications were discussed. In many of the above materials, that are representatives of many others find in the literature, a diversity of transient and steady state processes was possible to devise, with time scales from picoseconds to many hours or years. The potential use of time-resolved and variety of types of pump-and-probe experiments to unveils the details of the dynamics of the charged carriers were discussed in view of the future potentials in the Sirius storage ring.

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KEYWORDS: EXAFS, XANES, XEOL, LUMINESCENCE, TIME-RESOLVED

Oral Presentation

SMALL MOLECULE SINGLE CRYSTAL X-RAY DIFFRACTION STUDIES AT THE MX2 BEAMLINE OF THE LNLS: CRYSTAL ENGINEERING OF ORGANIC MOLECULES AND COORDINATION COMPOUNDS WITH RELEVANCE TO MATERIAL SCIENCE

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Crystal engineering is a discipline that has as main interests the design and synthesis of crystalline solids with a particular purpose and specific properties [1]. Thus, as a starting point, it is essential to perform high quality single crystal X-ray diffraction studies that conduct successfully to the determination of the molecular and supramolecular structure of the studied systems. The instrumental limitations of laboratory single crystal X-ray diffractometers restrict significantly the projects related with crystal engineering and structural chemistry. Data collection at a storage-ring synchrotron source opened new possibilities for crystal structure determinations bringing enormous advantages for fields related to small molecules building blocks, like crystal engineering, as well as chemical and materials science areas in general [2]. In this work we will present the single crystal X-ray diffraction structural studies of several small molecule systems performed by the data obtained using the MX2 beamline of the LNLS. We were able to successfully determine the structure of several members of the following systems: a) organic molecules which are able to act as building blocks for the construction of different materials such as, supramolecular gels and mesocrystals; b) mononuclear and polynuclear coordination compounds and c) coordination polymers (CP). The coordination systems included in b) and c) were mainly synthetized using the molecules mentioned in a), as ligands. In all cases the information obtained contributed to unequivocally confirm their molecular structure and study their supramolecular characteristics and properties. These results were also fundamental to analyse the role of the structural features and intermolecular interactions in the crystal packing and also, in the physical and chemical properties. Regarding the compounds included in system a), new chiral molecules derived from amino acids and platforms like aldehydes were synthesized in our group for the development of different type of materials such as, supramolecular gels [3] and mesocrystals, a fascinating class of crystalline nanostructured materials [4]. With the data obtained from the MX2 beamline, it was possible to study the single crystals of several amino acid derivatives and successfully determine their structure with excellent resolution. These results contributed to the understanding of the mechanism related to the gel formation and mesocrystals aggregation. On the other hand, some of these molecules were used as ligands for the synthesis of coordination compounds –systems b) and c)–, exhibiting different physical and chemical properties. For instance, with the data collected at the LNLS it was possible to determine the X-ray diffraction structure of a trinuclear Ni(II) complex based on a L-Tyrosine derivative, several mononuclear amino-acid based Cu(II) monocuclear complexes and 1D Cd(II) and Co(II) coordination polymers. Finally, some of the physical and chemical properties of these coordination compounds are also discussed in term of their structural features.

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Keywords: Small molecule crystallography, Crystal engineering, Amino acids

ORAL PRESENTATION

SOFT X-RAY PTYCHOGRAPHY OF MAGNETIC DOMAINS – PROMISES AND LIMITATIONS

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We report on recent experimental work performed at the Advanced Photon Source (ALS) of an attempt to image in 3D a range of magnetic nanostructured thin films (~100nm thickness) including skyrmions, stripe and worm domains at nanometer resolution, with the aim to obtain maps of their domain wall structures at as high a resolution as possible. This experiment was motivated by the recent work of Donnelly et al [1], where hard X-ray vector tomography was performed to 100nm resolution on a micrometer thick sample. Our work was unfortunately limited by a lower than optimal source brightness, reducing the maximum resolution obtainable to the 20-40nm range, outside of what would be necessary to satisfactorily study the domain wall morphology. The Advanced Light Source however is a fairly mature instrument, and had this work been performed at SIRIUS, higher performance would have been expected due to diffraction limited coherent flux. A series of simulations will be presented to evaluate the expected possibilities of such an experiment at SIRIUS, looking at expected scattered photon counts for different magnetic samples and the resulting sample heating from high photon incidence, thus providing a realistic evaluation of experimental possibilities in the near future.

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KEYWORDS: PTYCHOGRAPHY, MAGNETIC DOMAINS, SOFT X-RAY RESONANT SCATTERING

POSTER PRESENTATION

SPUTTERING GROWTH OF ORDERED ALLOYS UNDER CONTROLLED MAGNETIC FIELD AND ITS EFFECT ON STRUCTURE AND MAGNETISM

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The use of magnetic thin films in information technology shows a growing importance in the past few decades, first applied to magnetic recording medias [1] and more recently in spintronic devices [2]. The new generation of hard disks uses perpendicular magnetic anisotropy (PMA), with heat assisted writing technology [1, 3]. In this context, it is relevant to study materials with high magnetocrystalline anisotropy, such as ferromagnetic chemically ordered alloys [1] (e. g. FePt, CoPt, FePd, CoPt, FeNi). Here, we concentrate at the FePt alloy. The L10 chemically ordered phase of FePt alloy shows the highest magnetocrystalline anisotropy among the transition metal alloys [4]. However, FePt alloy typically present a chemically disordered structure and deposition under high temperatures, above 600 °C, are required to give rise to the L10 phase. It has been observed thin film FePt with chemical order L10 grown on both (SiO_2/Si(100)) and MgO(100) substrates at 600 °C [5]. Furthermore, it is also possible to obtain ordered FePt by applying a magnetic field during postdeposition anneling [6]. Here we propose to investigate the effect of applying a controlled magnetic field during the deposition of FePt films by sputtering technique. For each deposition condition (temperature, substrate and stoichiometry), three samples with distinct field configurations are grown simultaneously: one with 0.39 T applied perpendicular to the substrate plane, one with 0.39 T applied along the substrate plane and the third one without magnetic field (< 0.0026 T). This is achieved through a new instrumentation we have developed at the LMF AJA sputtering of LNNano, using SmCo high temperature permanent magnets (T<300°C) with in-plane and out-of-plane configuration and soft magnet steal for magnetic shielding (near zero-field position). Associating this new instrumentation with structural (XRD, SEM, AFM) and magnetic (VSM, PPMS, SQUID) characterizations we aim to contribute to the fundamental understanding of the effect of the magnetic field on the chemical ordering of such alloys during growth, with possible impact on its applications. In this poster we give details of the developed instrumentation and expose the first results of FePt growth under magnetic field.

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KEYWORDS: MAGNÉTIC THIN FILMS, SUPETTERING, FEPT, XRD, MAGNETISM

ORAL PRESENTATION

STABILITY OF (LA-NI-CO-O)-BASED PEROVSKITES IN LPG STEAM REFORMING: ASSESSMENT OF GAS COMPOSITION AND NI/CO RATIO

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Steam reforming of Liquefied Petroleum Gas (LPG) is a viable option for producing hydrogen in isolated regions [1]. Catalysts prepared from perovskite precursors may retain metal particles dispersed and decrease sintering due to the high interaction particle-support [2], but even so the oxidation rate of carbon deposits is still high [3]. Partial substitution of Ni or Co in the B-site of ABO_3-type perovskites may increase reducibility and stability while maintaining high hydrogen yield [4]. In order to understand the reasons for high carbon deposition rates on these catalysts and to attempt to control the deposition process, Ni/Co bimetallic catalysts synthesized from La-based perovskite precursors were tested for LPG steam reforming. IN-SITU XRD analyses showed that, depending on the fraction of substituted Ni, the perovskites go through one or two reduction steps before decomposing into bimetallic Ni/Co particles supported on La_2O_3. EXAFS data indicated that the nanoparticle's surface are enriched with Co after reduction, but Ni atoms migrate to the surface and overlay the former Co shell soon after feeding the LPG steam reforming mixture. In samples synthesized with low Co/Ni ratio, the Ni surface layer oxidizes after a few hours during reaction operation, showing signs of deactivation. Oxidation could be prevented by decreasing the water/LPG feed ratio, which reactivated the catalyst. The use of a proper water/LPG feed ratio coupled with the suitable Co/Ni ratio in the synthesis of perovskite precursors is essential to keep the catalysts active during LPG steam reforming.

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KEYWORDS: LPG REFORMING, NI/CO PEROVSKITE, EXAFS, NI OXIDATION, DEACTIVATION RATE

POSTER PRESENTATION

STRUCTURAL CHARACTERIZATION OF A NOVEL ANTI-INFLAMMATORY N-METHYL-N-ACYLHYDRAZONIC DERIVATIVE

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Studies leading to a greater comprehension of biologically active compounds in the solid state play a key role in the synthesis of new drugs. As important as the design and synthesis of new drugs is their structural characterization; exploring the arrangements of molecules in crystals provides a path to the design of new compounds and to the elucidation of processes in which a molecule recognizes a particular biological target [1]–[2]. In this work, we determined the crystal structure of LASSBio-1366 with X-ray powder diffraction (XRPD) data. This compound was planned and synthesized in the Laboratory of Evaluation and Synthesis of Bioactive Substances – LASSBio® of the Federal University do Rio de Janeiro (UFRJ) as part of a research program to develop a series of compounds with anti-inflammatory properties [1]. LASSBio-1366 is a N-methyl-N-acylhydrazonic derivative inhibitor of PDE4 and TNF-α in vitro and also active in LPS-induced inflammation models in vivo, thus it can be highlighted as anti-inflammatory prototype compound inhibitor of PDE4 [1]. The XRPD were recorded at room temperature on a STADI-P powder diffractometer (Stoe®, Darmstadt, Germany) and the crystal structure determination procedure of the LASSBio-1366 was performed both by indexing and decomposing the powder pattern using the Topas Academic v.5.0 software program [3] via a Pawley fit [4] and the space group was determined as being Pbca. The cell volume found in the indexing procedure suggested eight molecules per unit cell (Z = 8) and one molecule in the asymmetric unit (Z´ = 1). Subsequently, the Rietveld refinement [5] of the final crystal structure was conducted using the Topas Academic v.5.0 software program. The Rietveld method was used to refine the crystal structure and the goodness-of-fit indicator as well as R-factors were χ2 = 1.516, RBragg = 1.974%, Rwp = 2.475% and Rexp= 1.632%. The crystal structure of LASSBio-1366 allowed us to show structural aspects of the composite solid phase allowing the characterization of the relative configuration E of the imine double bond. Our goal is to continue performing the structural characterization of polycrystalline compounds and for this we can use Paineira beamline on Sirius at the Brazilian Synchrotron Light Laboratory.

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KEYWORDS: STRUCTURE DETERMINATION, N-METHYL-N-ACYLHYDRAZONIC, PHOSPHODIESTERASE-4 INHIBITOR

POSTER PRESENTATION

STRUCTURAL CHARACTERIZATION OF $LA_{0.8}AE_{0.2}MNO_{3+\Delta}$ (AE = CA, SR, BA) PEROVSKITES FOR CATALYTIC OXIDATION OF VOLATILE ORGANIC COMPOUNDS

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Perovskite oxides have the general formula ABO_3, where A is typically an alkaline earth (AE), lanthanide or other large cation and B is a smaller cation like transition-metals. This family of compounds are probably the most studied materials in the last decades since understanding the correlation between their structure and properties is of fundamental and technological interest [1]. Despite the simplicity of the crystalline structure, the fact that A and B can be almost any cation of the periodic table creates an immense structural variety and originates numerous deviations respect the ideal structure through changes in the crystal symmetry, that leads to the appearance of interesting properties such as multiferroic properties (magnetic, electric, elastic, etc.). At the moment, the most alluring applications that make use of these structures are: energy conversion (fuel cells, electrolyzers), adsorption and catalysis (mainly heterogeneous), among others. A few years ago, the catalytic oxidation combustion process involving perovskite-based catalysts –especially manganites- arose as an interesting alternative to traditional methods for Volatile Organic Compounds (VOCs) elimination. VOCs are a group of carbon-based chemicals considered not only as major contributors to air pollution but also one of the main hazardous substances for human health. An additional complication, is that this category of pollutants includes a wide range of compounds with very different chemical properties, what makes it difficult to find a single catalyst for the effective elimination of all of them [2]. In this work we present results on synthesis, characterization and acetone conversion (%) for $LaMnO_3$ and the $La_{0.8}AE_{0.2}MnO_3$ series (AE= Ca, Sr, Ba). All of the compounds of the series were obtained as unique phases (see Figure) and used as catalyst as-obtained or fired at 750°C for 8 hs. All of them performed similarly when tested for acetone catalytic oxidation (the new materials proved to be active even at low temperatures: 17% conversion at 100°C for $LaMnO_3$), showing values comparable to those obtained in literature [3]. $La_{0.8}Ca_{0.2}MnO_3$ was the one which exhibited the largest difference between the as-obtained and calcined catalyst. The data obtained so-far has not been sufficient to understand the difference in the catalytic properties, so we will explore further characterization techniques that might be the key to explain these variations.

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KEYWORDS: PEROVSKITES, CATALYSIS, VOC

POSTER PRESENTATION

STRUCTURAL CHARACTERIZATION OF THE FULL-LENGTH BACTERIOPHYTOCHROME XCCBHPP IN THE PR AND PFR STATES

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Bacteriophytochromes (BphPs) are part of the phytochrome superfamily of photoreceptors. BphPs are proteins that bind biliverd in (BV) as their chromophore and typically present two photostates: a primarily red-absorbing form (Pr) and a far-red-absorbing form (Pfr) [1]. The phytopathogenic bacterium Xanthomonas campestris codes for a single bacteriophytochrome photoreceptor (XccBphP) that bears a photosensory module (PAS2-GAF-PHY domains) anda C-terminal PAS9 output module. This microorganism is able to regulate its virulence by sensing red and far-red light through XccBphP [2]. We have crystallized [3] and determined the structure of the dimeric full-length XccBphP in its red-absorbing state (Pr) at 3.25 Å resolution [4]. Very recently, we have also solved the crystal structures of the photosensory module alone (ΔPAS9) in its far red-absorbing state (Pfr) at 2.90 Å resolution and a full-length Pfr-stabilized XccBphP mutant variant at 2.50 Å resolution. These structures significantly help us to acquire a more comprehensive understanding on the long-range structural signaling in a full-length bacteriophytochrome at the atomic level.

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KEYWORDS: XANTHOMONAS CAMPESTRIS PV. CAMPESTRIS, BACTERIOPHYTOCHROME, LIGHT-SIGNALING PATHWAY, PHOTOSENSOR, SIGNAL TRANSDUCTION

POSTER PRESENTATION

STRUCTURAL FEATURES OF A NEW CARBOXYLIC ESTER HYDROLASE FROM *BACILLUS LICHENIFORMIS*

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Carboxylic ester hydrolyses (EC 3.1.1.x) are enzymes that act on ester bonds, either hydrolysis or esterification reactions. They are widespread in nature, being expressed by animals, plants and microorganisms, and playing an essential role in the metabolism of the endogenous e exogenous carboxyl esters like fat acids, triacylglycerols, xenobiotics, environmental pollutants and drugs [1]. Besides the important physiological functions, they compose one of the most important biocatalysts for biotechnology, being widely applied on a broad range of industrial applications and with many available commercial preparations [2]. Bacillus licheniformis is a microorganism commonly used in various industrial and biotechnology industries as well as being a promising source of esterase [3]. However, up to date, there is no structural information regarding *B. licheniformis* carboxylesterases. After trials for crystallization conditions using different commercial kits, BlEst2 crystallized in a PACT Suite (Molecular Dimensions, USA) condition, which was optimized to 0.2 M calcium chloride, 0.1 M Tris pH 8.0 and 28% (w/v) polyethylene glycol (PEG). Then, a single crystal was submitted to the x-ray beam line MX2 of the Brazilian Synchrotron Light Laboratory (LNLS, Campinas). The crystal structure of BlEst2 was determined by single anomalous diffraction using iodine ions for obtaining anomalous signal. Data was indexed in the orthorhombic space group P212121 and two molecules were predicted in the asymmetric unit. Model was refined at 2.0 Å resolution, and final model showed Rwork/Rfree values of 0.19/0.22, and about 98% of residues inside Ramachandran's favored. Final model was built from residues 28-482. BlEst2 presents the core region with a typical α/β hydrolase fold and an overall multidomain structure. Despite its sequence divergence, BlEst2 catalytic core at domain I is very similar to other known single domain lipases and the position of the key catalytic residues, Ser119, Asp231 and His254, is conserved between the proteins. Besides this, domain I presents two insertions, which occupy conserved locations in α/β-hydrolase proteins and commonly made up the lid domain on lipases. However, the extra domains II and III located on the enzyme C-terminus are not similar to any know structural motif of carboxylesterases. These findings suggest that BlEst2 might compose an unclassified group of carboxyl ester hydrolases and motivate us to continue the structural studies until we figure out the role of the additional domains.

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KEYWORDS: CARBOXYLIC ESTER HYDROLYSES, BACILLUS LICHENIFORMIS

POSTER PRESENTATION

STRUCTURAL REFINEMENT OF THE ENZYME TRIOSEPHOSPHATE ISOMERASE FROM *NAEGLERIA GRUBERI*

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Triosephosphate Isomerase (E.C. 5.3.1.1) (TIM) takes part in the glycolytic pathway, converting substrate dihydroxyacetone phosphate (DHAP) to glyceraldehyde 3-phosphate (G3P). *Naegleria gruberi* (Ng) is a free-living protist that can be found in environments like lakes, humid soils and mud. This organism has been studied with the aim of comprehending better free-living eukaryote evolution. The enzyme gene was inserted into a pET-15b plasmid to be overexpressed in Escherichia coli. After growth for 16 h at 37°C, the cells were disrupted and the protein was purified by IMAC. The enzyme was concentrated to 3.5 mg mL^{-1} and crystals were obtained by the hanging drop vapor diffusion method. X-ray diffraction experiments were carried out station MX2 of the Brazilian Synchrotron Light Laboratory (LNLS). Some crystals with quality for structure determination were observed. Still, one particular condition, Jeffamine® M207 30% (V/V), 0.2 mol L^{-1} of KCl and Tris buffer 0.1 mol L^{-1} pH 8.0, provided a dataset to 1.74 Å resolution at MX2. The final refined structure presents the typical TIM barrel fold. Electron density for one Tris and one Jeffamine molecules were observed and these were modeled accordingly. Some indeces for the final model were: R = 15.50%, Rfree = 20.45%, rmsd bond lengths = 0.008 Å, rmsd bond angles = 1.064°, with 252 aminoacids, none in disallowed regions according to the Ramachandran plot. In general, a good fit of the model to the electron density was observed, (RSCC = 0.956 and RSR = 0.134). The model comprehends a dimer in the asymmetric unit, with solvent content of 43.3%. The enzyme structure shows the typical fold of Triosephosphate Isomerases. Structural and sequence comparison will be accomplished to search for particular features.

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CAPES and Laboratório Nacional de Luz Síncrotron.

KEYWORDS: NAEGLERIA GRUBERI, TRIOSEPHOSPHATE ISOMERASE, PRIMITIVE EUKARYOTE

POSTER PRESENTATION

STRUCTURAL STUDIES IN XYLOSE ISOMERASE USING SYNCHROTRON RADIATION

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Xylose Isomerase (XI) plays a key role in monosaccharide isomerization. It catalyzes aldose – ketose interconversion from sugars of 3, 4, 5 and 6 carbons [1], characteristic which makes XI very important for industrial purposes [2]. There are currently several research projects aiming to optimize XI processes, particularly HFCS production (glucose – fructose conversion) and Second Generation (2G) Ethanol (Xylose – Xylulose conversion). Recent studies have been conducted in order to characterize XIs from different sources, in order to find the best candidate for Industry [3,4]. Within this search for potential candidates, many microorganisms have been drawing attention for their natural characteristics, such as heat and salt tolerance, and the ability to degrade complex polysaccharides. The XI from this study is from a marine microorganism isolated from salt marsh, capable of living at 30°C (near the industrial fermentation temperature) and degrades several polysaccharides [5]. The biochemical essays were conducted, and enzymatic parameters were defined. KM and Kcat values were consistent to other XIs characterized. The crystallographic structure was determined by X-ray crystallography, using MX2 beamline in LNLS. The enzyme presented the usual topology for XIs: The N-terminal TIM-barrel like domain, with the active site, and a C-terminal loop-helix-loop domain. Enzymatic data showed that XI is a very thermal stable enzyme, so, structural studies using small angle x-ray scattering (SAXS) were performed in order to investigate the oligomeric state in solutions, and the heating effect in XI. The enzyme presents itself as a tetramer in solution, and the heat increasing up to 70°C showed no significant modifications, such as dimer or monomer formation. These results obtained revealed that XI is a very compact and cohesive tetramer, with strong bonds within the interfaces. The mechanism [6] and the active sites are known and conserved within the family, and further studies shall be conducted in order to understand better the oligomerization hierarchy within this enzyme group.

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CAPES, IFSC-USP, CNPEM

KEYWORDS: XYLOSE ISOMERASE, X-RAY CRYSTALLOGRAPHY, SAXS

ORAL PRESENTATION

STRUCTURAL, ELECTRONIC AND MAGNETIC CHARACTERIZATION OF SRTIO$_3$/LA$_{0.67}$SR$_{0.34}$MNO$_3$/FE-PHTHALOCYANINE/CO

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Understanding how to incorporate organic materials in spintronic devices is still a frontier research in spite of intensive investigation. Several organic spin-valves have been designed as two magnetic electrodes sandwiching an organic film that displayed magneto-resistive behavior [1]. Here, we investigated Co(0.5nm)/FePc(~1nm)/La$_{0.7}$Sr$_{0.3}$MnO$_3$(~60nm)/SrTiO$_3$ multilayered sample. LSMO and Co are the most used electrodes for organic spintronics, in particular LSMO has a stable surface to oxidization and excellent magnetic polarization at room temperature. FePc is a quasiplanar heterocyclic macrocycle molecule with high conjugation, already showing FM order when in contact with Co FM film [5]. The heterostructure was prepared using the surface facility tools (Pulser Laser, Organic and Inorganic Molecular Beam Deposition Chambers) and characterized (X-ray Photoemission and Absorption) IN-SITU at PGM beamline, LNLS. The chemical interaction between FePc and Co has been observed as modification of X-ray core level (C 1s and N 1s) and absorption (at Fe and Co L2,3) spectral line shapes. The magnetic response of each component of the heterostructure was monitored by X-ray Magnetic Circular Dichroism, whereas the overall magnetic properties are probed with a vibrating sample magnetometer. Each component show ferromagnetic coupling, however the overall magnetization presents the signature of spin reorientation at temperature between 2 and 100K. These results help in understanding the control of magnetic properties of hybrid organic/inorganic heterostructure.

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KEYWORDS: MAGNETISM, HYBRID ORGANIC-INORGANIC HETEROSTRUCTURE

POSTER PRESENTATION

STRUCTURE OF ELECTRODEPOSITED PRUSSIAN BLUE LAYERS

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Prussian Blue (PB) and its reduced form Prussian White (PW) were prepared by electrochemical synthesis, by varying the deposition voltage and thickness. Thick, compact and uniform layers were characterized by electron microscopy, X-ray diffraction, X-ray absorption spectroscopy, and Raman spectroscopy. Results have shown a well-defined transition voltage for growing these Prussian Blue phases and a strong dependence of the morphology/growing orientation of the deposits on the applied potential and thickness. For the negative potential of -0.10 V vs. SCE a mixture of cubic and rhombohedral phases was observed. The transition from cubic to rhombohedral is investigated in samples prepared under different deposition conditions. In parallel, the samples were submitted to charge and discharge cycles for the incorporation and release of K ions and also other intercalation ions such as Na and Li. Prussian Blue and analogs have been considered more recently as potential materials for sustainable energy storage devices.

KEYWORDS: PRUSSIAN BLUE, PRUSSIAN WHITE, ATOMIC STRUCTURE, INTERCALATION

POSTER PRESENTATION

STUDY OF ANTIBIOTIC PEPTIDE INTERACTION WITH BACTERIAL MODEL MEMBRANE SYSTEMS BY GIXOS

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Bacterial membranes are interesting as case of study of lipid interaction in biomembranes as they are formed by a few classes of phospholipids. In addition, antibiotic peptides produced by members of all kingdoms of life affect membrane permeability as a principal part of the mechanism of action. In the present work we explored the role of membrane composition of Gram positive model systems on the interaction with the bacteriocin enterocin CRL35 by means of Langmuir monolayers and Off-Specular X-Ray diffraction at grazing incidence (GIXOS). Lipid mixtures used were PG:PE 80:20 and CL:PG:PE 40:40:20, in order to study Gram positive mimics and the role of cardiolipin in membrane properties and peptide interaction. Affinity of enterocin to lipid films was assessed by calculating exclusion surface pressure and monolayer structure mainly by determining the minimum of the first lobe of GIXOS pattern for getting insight of monolayer thickness. Results indicate that cardiolipin modulates affinity of enterocin towards bacterial lipids and diminishes monolayer thickening upon peptide interaction.

ACKNOWLEDGEMENTS

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KEYWORDS: LANGMUIR MONOLAYER, BACTERIAL LIPIDS, ANTIMICROBIAL PEPTIDE, GIXOS

POSTER PRESENTATION

STUDY OF GRAPHENE OXIDE DISPERSIONS WITH DIFFERENT OXIDATION DEGREES BY SMALL-ANGLE X-RAY SCATTERING (SAXS)

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Graphene oxide (GO) is the most important derivative of graphene, produced by liquid phase exfoliation of graphite oxide, based in a modified Hummers method [1]. This material presents a two-dimensional structure, consisting of less than ten layers of carbon [2]. Interplanar distance between GO layers may be variable from 0.62 to 1.2 nm in a dried GO [3], determined by X-ray diffraction (XRD). Thickness of these GO monolayers are about 0.8 nm [4], measured by atomic force microscopy (AFM). However, the behavior of this material in water dispersion is completely different from the dried one, such as the organization of GO flakes in liquid crystal mesophases in water [5]. Small-angle x-ray scattering (SAXS) is a technique that permits the study of a system in terms of size and shape [6], so that it is possible to obtain a large number of characteristics from GO flakes, even the thickness and the interplanar distance of the layers [7]. In this work, GO dispersions were produced with different oxidation degrees (4 hours, 1 day, 3 days, 7 days and 10 days) [8] and variable volume fractions (0.29%; 0.51%; 1.02% and 1.53%). The samples were sonicated and then analyzed by SAXS in SAXS1 bean line on UVX facility from the Brazilian Synchrotron Light Laboratory (LNLS). From 2D scattering patters and the profiles of scattering and their analysis, it was possible to obtain the scattering vector (q0), the interlayer spacing (d001), and then the experimental thickness of GO sheets. The values obtained were compared with those extracted from XRD and AFM.

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KEYWORDS: SAXS, GRAPHENE OXIDE, THICKNESS

Poster Presentation

STUDY OF PH VARIATION EFFECT ON CDSIO$_3$ LUMINESCENCE PRODUCED BY THE SOL-GEL ROUTE

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The search for new luminescent materials for application in different areas is becoming more and more intense, as these materials are increasingly present in everyday life, such as in TVs, in the detection of diseases through images, in electronic devices, lighting systems and scintillators for radiological protection [1,2]. In this sense, studies of cadmium silicate matrix have been extensively investigated especially because of its ease incorporation of dopants into its network, creating different structural defects which in turn leads to luminescence in different colors and lifetimes. The hole of synthetic parameters such as pH sol on defect production and, consequently, the luminescent mechanism associated with the defect structure is still an open question. Aiming to contribute with this relevant field, this work presents the luminescence characterization performed at high and low temperatures of $CdSiO_3$ powders. The materials were prepared by Sol-Gel process with the pH of departing sol adjusted to 1, 7 and 9, and calcination temperature of 1000°C for 3 h. Emission and excitation spectra were recorded on the TGM beamline (proposal #20190133) using a setup that allowed to achieve temperatures in the range of 60 K. Preliminary results showed two emission bands, the first with a maximum of approximately 400 nm and the second centered at 580 nm. As the temperature was approaching 60 K, the extinction of the 580 nm-band was observed. The relative intensity of the two emission bands also varied with the pH values of the studied samples.

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Keywords: CdSiO3, pH, Sol-gel

POSTER PRESENTATION

STUDY OF PLANT SPECIES FOR REMEDIATION OF PB-CONTAMINATED SOIL BY SYNCHROTRON RADIATION X-RAY FLUORESCENCE MICROSCOPY AND INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY TECHNIQUES

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Synchrotron-based X-ray fluorescence microscopy (SR micro-XRF) and Inductively coupled plasma mass spectrometry (ICP-MS) techniques are increasingly being used in soil-plant systems to evaluate toxic metals with important applications on environmental sciences [1,2]. SR induced micro-XRF is an innovative technique that allows the mapping of the distribution of a wide range of elements in vegetable tissues. At the same time, ICP-MS allows the multi-elemental analysis reaching detection limits lower than ppb levels. The aim of this work was to study the potential use of *Brassica napus* (Bn), Festuca arundinacea (Fa) and Lolium perenne (Lp) for the remediation of Pb contaminated soils. Bn, Fa and Lp were grown at two levels of Pb in soil (Basal and 1000 ppm) in controlled conditions (greenhouse) during an annual cycle. To study how Pb and others elements from the soil are uptaken and translocated by the plant, SR micro-XRF was performed to determine the spatial distribution of the chemical elements present in roots and leaves. The measurements were carried out at the D09BXRF beamline of the Brazilian LNLS, on different parts of the living plant. Additionally, after the harvest, the biomass value in dry weight was obtained and the Pb concentration was determined in roots and leaves of each species by ICP-MS at the National University of Córdoba (UNC) and CEPROCOR. SR micro-XRF results showed that, in living conditions and early periods of plant growth, Bn extracted Pb from the ground and translocated it to the leaves more effectively than Fa and Lp. Furthermore, a co-distribution was observed between Pb and Zn, P, S, and Fe. Besides, ICP-MS Pb concentration of aerial parts and roots of the plants were used to calculate bioaccumulation factor (BAF) and Pb total extraction (PbTE). ICP-MS results showed that at the end of an annual cycle period, for the plants that grew in soils contaminated with Pb, significant differences were obtained in the PbTE and BAF ($p < 0.003$) for Fa in relation to Bn and Lp. No significant differences were observed ($p = 0.82$) in the PbTE between Bn and Lp. This suggests that Fa is a fast growing plant that could be used to remediate Pb contaminated soil. The complementary use of these two techniques enables substantial advances in several disciplines of plant science since it allows to study possible mechanisms involved in metal(loid) uptake and estimates the ability of the phytoremediation process.

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KEYWORDS: SR MICRO-XRF, ICP-MS, PHYTOREMEDIATION, LEAD

Poster Presentation

STUDY OF THE MORPHOLOGY AND ORIENTATION OF MESOSTRUCTURED SYSTEMS BASED ON AMINO ACIDS DERIVATIVES BUILDING BLOCKS

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Recent studies show that small molecules based on amino acid derivatives are able to assemble into ordered superstructures, also called mesocrystals [1], when they are subjected to certain crystallisation conditions. The control over experimental parameters as pH, supersaturation level, ionic force and the use of additives, are some of the most popular approaches [2, 3] to obtain this new kind of material. Besides, due to its rich supramolecular chemistry, self-assembly strategies applied to some low-molecular weight building blocks can conduct to other kinds of solid materials, such as supramolecular gels. In this case, their properties can be modulated by variation of temperature or solvent, since these changes directly affect the strength of the non-covalent interactions within the gel network [4]. The development of a spanning network that can immobilize solvents or the self-assembly between the building blocks, are both governed by the presence of non-covalent interactions. Thus, there is a delicate balance for a low-weight molecule to behave as a gelator or, as a crystal building block. In the present work we analysed the physiochemical factors implied in the obtaining of different self-assembled structures such as gels and mesocrystals, in a new family of quiral small molecules based on the aryl amino acids L-Tyrosine and L-Phenylalanine. The resultant supramolecular structures and their physicochemical properties were studied by different spectroscopic techniques, X-ray diffraction (XRD), small angle X-ray scattering (SAXS), polarized light microscopy (PLM) and scanning electron microscopy (SEM). Moreover, we studied the preferential crystalline orientation within a single polycrystalline aggregate (mesocrystal) obtained under different synthesis conditions. These measurements were possible due to the advantages offered by the large area detector and the high-intensity collimated beam of the MX2 beamline at the LNLS. Diffraction patterns were collected under this experimental set up, which allowed the study of the characteristic systematic absences of the material. Powder-like diffractograms were obtained applying a radial integration of the data in the azimuthal angle using GSAS-II software. Based on the fact that, as mesocrystal orientation respect to beam is changed, systematic absences are also altered, we were able to study the structuration of the material along with their different morphologies. As expected, when a spherical-like mesocrystal was analysed, no systematic absences were observed. On the other hand, depending on the orientation of a rod-like aggregate, systematic absences were detected. These valuable results are a direct characterization of the hierarchy of the structuration of the material and together with the information derived from other techniques, allowed us to elucidate putative mechanisms of the self-assembly based on the crystallization conditions.

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Keywords: Mesocrystals, Amono acids, MX2 beamline

POSTER PRESENTATION

STUDY OF THE REACTION KINETICS OF ORGANOSULFUR COMPOUNDS OXIDATION BY ATOMIC CLUSTERS

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Catalysis is one of the main areas concerning industrial and scientific relevance. The fact that 75% of all chemicals —90% of newly developed processes— are produced using catalysts highlights the importance of catalysis in the chemical industry. In particular most of the processes involved in crude-oil processing and petro chemistry, such as refining and chemical transformations, require catalysts. Environmental protection measurements, such as elimination of exhaust gas from automobiles and industrial plants, would be inconceivable without catalysts [1–3]. The key factor in catalysis is to find, for each reaction, materials with high activity, selectivity and stability. However, it's difficult to find catalysts that completely fulfill these three requirements. AQCs with a few atoms (less than ≈50 atoms) represent a novel state of matter, with properties completely different from nanoparticles (NP), and strictly dependent on the number of atoms. This is due to the quantum confinement of the free electrons, that causes the discretization of energy levels and, consequently, a change in their physicochemical properties that differs strikingly from what would be expected from a simple extrapolation of their properties from their NP counterparts. Contrary to what would be expected, AQCs possess a surprising high chemical and thermal stability, superior to the bulk material, as reported by the Buceta Fernández *et al.* [4]. Recent results obtained shows that Ag5 AQCs display high catalytic activities for the fully aerobic oxidation of different types of sulfur species to sulfates at room temperature. This occurs even for the most complicated aromatic thiols to be oxidized in the industrial field, such as asphaltenes [5] In this work we present a study of the kinetics of the oxidation reaction for different types of sulfur groups, produced by Ag or Cu AQC, by measuring IN-SITU the S-K edge XANES using a cell constructed ad-hoc. This study allows determining for example that there are at least two steps in which the oxidation of cysteine by Ag AQC occurs, first one that goes from the cysteine to some kind of disulfide and then in step two it goes to sulfate species.

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KEYWORDS: XANES, CLUSTERS, SULFUR

POSTER PRESENTATION

STUDY OF TRACE ELEMENTS CONCENTRATION AND ELECTRON DENSITY VARIATION IN CANINE MAMMARY TUMORS

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Mammary neoplasms are the most common in female dogs, with malignancy rates of approximately 50% [1]. Similarities between human and canine breast tissues, indicates dogs as a suitable model for human breast cancer [2]. Studies have shown that changes in the concentration of trace elements can be related to pathology development in tumorous tissues [3]. A widely reported technique for mapping the spatial distribution of trace elements is Micro X-ray fluorescence (µ-XRF) [3]. Similarly, the Compton scattering technique allow assessing the electron density of samples, providing information about the tissue matrix [4]. In this work we combined both techniques; µ-XRF for mapping the spatial distribution of Fe, Cu and Zn, and Compton scattering for determining the electron density of 7 canine mammary tissues (2 normal, 2 benign and 3 malignant). For the µ-XRF experiments, the samples were positioned at 45 degrees with respect to the incident beam, on an XYZ table. They were scanned with a white beam collimated with 30 µm of internal diameter, in 0.04 mm steps, with spectra acquisition time varying between 200 ms and 400 ms for each sample. For the Compton scattering measurements, the experimental arrangement was modified with the addition of a Si (111) double crystal monochromator, used to select an energy of 12 keV. Four to six points, encompassing healthy and neoplastic tissue, were chosen for each sample, and measured 5 times each with 200 seconds cycles. Results showed an accumulation of Fe in regions of blood vessels for all measured samples. For the malignant ones, this increase was observed in tumor-adjacent regions, but not in the tumor region itself. In addition, one sample presented a higher value of Cu in the tumor region. For normal tissues, Cu and Zn were homogeneously distributed throughout the sample, with lower concentrations in adipose regions. In the benign neoplasms, one of the samples presented a significant increase in Cu concentration, with a similar behavior in the second sample, albeit in smaller proportions. The electron density values obtained allows differentiate the various structures of tissues, and most values agreed with the literature for human breast tissues, being higher in tumor regions and lower in the adipose tissue areas. Therefore, the combination of µ-XRF and Compton scattering is an effective tool for obtaining complementary information regarding canine mammary tumors.

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KEYWORDS: CANINE MAMMARY TUMORS, X-RAY FLUORESCENCE, COMPTON SCATTERING

POSTER PRESENTATION

SUPERELASTIC NITI SHAPE MEMORY ALLOY IN-SITU THERMOMECHANICAL SIMULATION BY GLEEBLE® SYNCHROTRON SYSTEM

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NiTi alloys have attractive functional properties as shape memory effect and the superelasticity appropriated to be used in different segments in engineering and biomedical areas, in addition to exhibit excellent corrosion resistance and biocompatibility. These functional properties are obtained through the thermomechanical process. Thermomechanical processes aim to obtain the appropriate shape of the material, to control phase transformation temperatures, to improve the alloy characteristics, and refine shape memory effect or superelasticity. To obtain the desired microstructure the hot work should be performed to assure the mechanical and functional properties adequate. In this study the physical simulation as to the evaluation of the structural modifications in the remelted and annealed alloy was performed at Gleeble® at two different deformation rates (of the order of 10^{-1} and 10^{-2} s^{-1}) at 850°C.

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The X-ray scattering and Thermo-Mechanical simulation (XTMS) experiment were carried out the XRD1 beamline, LNLS - CNPEM, Campinas - Brazil. The uniaxial compression tests were carried out on an advanced thermomechanical simulator, the Gleeble® Synchrotron system. The optical and electron microscopy were carried out the IME, Rio de Janeiro – Brazil.

KEYWORDS: NI-RICH NITI SHAPE MEMORY ALLOY, SYNCHROTRON RADIATION X-RAY DIFFRACTION (SR-XRD), GLEEBLE®

POSTER PRESENTATION

SYNCHROTRON RADIATION MICROTOMOGRAPHY (SR-µCT) FOR BIOLOGICAL APPLICATIONS AT IMX BEAMLINE

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Microtomography using synchrotron sources has become a useful tool in biological imaging research since synchrotron radiation properties enable SR-µCT to reconstruct highly resolved 3D image. Several applications using SR- µCT have been made by our group (some are still in progress) at IMX beamline-LNLS, among which we can highlight applications in insects, tadpoles and fishes. Among the most recent paper, we can highlight the use of SR-µCT to study the tadpoles [1], describing external and internal morphological features like cartilage, muscles, sacs containing calcium, crystalline and skin at a range of developmental stages. Another recent works deal with the insect *Rhodnius prolixus* , the most important vector of Chagas' disease [1-2]. In the first work [1] we investigated the effects of treatments with triflumuron in the ecdysis period (the molting of the R. prolixus cuticle). Images of this insect in such conditions have never been presented before. The other work [2] tested different staining methods in order to find the best protocol to study the nervous system of R. prolixus. Both works used IMX beamline-LNLS with pink beam and resolution of 1.9 µm. Other project is underway using SR-µCT: study of the internal anatomy of the small fishes, especially regarding the structures related to feeding and reproductive systems. With the new 4th generation light source (SIRIUS) we expect a wide range of new possibilities, allowing for much more sensitive analyses, grounding the collaborations between physics, biology, environmental and materials sciences.

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KEYWORDS: SYNCHROTRON, MICROTOMOGRAPHY, BIOLOGY

POSTER PRESENTATION

SYNTHESIS AND CHARACTERIZATION OF THE COMPLEX DIBROMO (N, N-BIS (2,6-DIETHYLPHENYL) -2,4-PENTANEDIMINE) NICKEL (II) AND APPLICATION IN THE ETHYLENE OLIGOMERIZATION REACTION

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The oligomerization of ethylene from the industrial point of view and the search for more active catalytic systems play an extremely important role, especially in the production of linear α-olefins, which are used as feedstock in the production of fuels, lubricants and surfactants[1-3]. Thus, the use of nickel β-diimine type precursors, which have high catalytic activity and selectivity to obtain light α-olefins is justified. In this work, the synthesis of a β-diimine linker using one amine with ethyl groups at positions 2 and 6 was also developed, a catalytic precursor was also synthesized using nickel as coordination metal, which was used in reactions in homogeneous oligomerization medium of the ethane, in order to obtain α-olefins. This catalytic precursor was tested in different molar ratios Al / Ni (50, 100 and 200), at a controlled temperature of 10°C and 15 bar of ethylene pressure. Reactions were made in triplicate. Catalytic precursor shown to be active in the ethene oligomerization reactions, with a higher selectivity for α-C4. The characterization techniques employed for the binder 1H NMR, elemental analysis of CHN and infrared (IV) and for the catalytic precursor also analyzed by infrared (IR) and X-ray absorption spectroscopy (XAS)[4]. The products of the oligomerization reactions were analyzed by gas chromatography.

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KEYWORDS: ETHYLENE, NICKEL COMPLEXES, HOMOGENEOUS MEDIUM

POSTER PRESENTATION

SYNTHESIS AND SYNCHROTRON CHARACTERISATION OF NOVEL DUAL-TEMPLATE OF CALCIUM PHOSPHATE SCAFFOLDS WITH CONTROLLED SIZE POROUS DISTRIBUTION

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Calcium phosphate scaffolds with a hierarchical porous architecture were prepared by a new dualtemplate (corn starch and cetyltrimethylammonium bromide (CTAB) surfactant) used to cast the calcium phosphate nanoparticles and development scaffolds with size hierarchical porous distribution. The powder X-ray diffraction (XRD) results showed that only the HAP crystalline phase is present in the samples after calcination; the Scanning Electron Microscopy (SEM) combined with Small Angle (SAXS) and Ultra-Small Angle X-ray Scattering (USAXS) techniques showed that the porous arrangement is promoted by needle-like nanoparticles, and that the pore size distributions depend on the drip-order of the calcium and the phosphate solutions during the template preparation stage.

KEYWORDS: CALCIUM PHOSPHATE, BIOMATERIALS, NANOPARTICLES, POROUS MATERIALS

POSTER PRESENTATION

SYNTHESIS OF SHAPE-CONTROLLED GOLD NANOPARTICLES BY SEED-MEDIATED GROWTH METHOD

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The carbon monoxide (CO) oxidation reaction, besides being considered as a prototypical to study the fundamental concepts of heterogeneous catalysis, is of high environmental and social importance. Gold used to be considered to have no catalytic activity because the inert nature of massive gold. However gold nanoparticles are highly active for CO oxidation and their catalytic activity can be improved by controlling its size and shape. To understand how those particles catalyzes a reaction is fundamental to investigate the facet-selectivity which offers different binding configurations and strengths [1]. The distinct atoms arrangement gives us many morphologies from rod, rectangle, hexagon, cube, triangle and others in the case of gold nanoparticles. Those various structures can be achieved by a systematic variation of experimental parameters in colloidal seed growth procedure to form Au nanoparticles. Our experimental methods involve, first, the preparation of Au seed particle. Gold (III) chloride hydrate ($HAuCl_4$), cetyltrimethylammonium bromide (CTAB) and sodium borohydride ($NaBH_4$) are used to prepare the seed. Subsequently, the growth of the Au particles is provided by addition of appropriate quantity of the Au seed solution with more CTAB, $HAuCl_4$, ascorbic acid (AA) [2] and water, giving us an aqueous solution. The size and monodispersity of the gold nanoparticles were analyzed by UVvis spectroscopy and Small Angle X-ray Scattering (SAXS). The result of the fit leads to seed nanoparticles with approximately 4 nm diameter and low polydispersity. The subsequent growth produced cubic and hexagonal shapes nanoparticles. From UV-Vis the average size is 61 nm and 73,5 nm for the cubic and hexagonal nanoparticles respectively. The gold nanoparticles solution was added to 100 mg of TiO_2 and acidified by H_2SO_4 (pH ~ 1) to obtain 1 % w/w of the catalyst. The samples were calcined in two-steps, 200 °C for 1h to CTAB decomposition then heated up to 400°C for 1h. The particle sizes and morphology were characterized by high resolution scanning electron microscopy operated in transmission mode with STEM detector (STEM). The distribution of particle sizes was 9,7 nm, 63 nm and 69 nm calculated by the measurement of 100 uniform particles in several selected STEM images for the seed, cubic and hexagon nanoparticles respectively. Removal of surfactant by thermal decomposition did not affect the shape neither the size distribution. In conclusion, the seed-mediated growth method using CTAB is a powerful strategy to produce nanoparticles with controlled morphology and dimension in very high yield for catalysis application.

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KEYWORDS: GOLD, SHAPE-CONTROLLED, CATALYSIS

POSTER PRESENTATION

THE SAGUI – SCATTERING ANALYSIS BEAMLINE

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The SAGUI – Scattering Analysis Beamline – is an undulator source beamline of SIRIUS second phase aimed to encompass the broad and numerous user community of X-ray scattering and diffraction that today uses SAXS1 and XRD2 beamlines of UVX machine. The design of the beamline optics and instrumentation follows from this requirement for versatility while taking full benefit of the great increase in brilliance at SIRIUS, being organized in three main experimental stations divided in two experimental hutches. The first hutch has an experimental station (42m) dedicated to Small and Wide Angle X-ray Scattering (SAXS/WAXS) in several sample environments (like SAXS1 at UVX), with the new requirement to include high throughput capabilities, both for liquids and solids, to reduce the loss of time between sample change and benefit from the flux gain. The second hutch features two experimental stations, one (53m) being a new 6+2 circles diffractometer for addressing usual XRD2 techniques (GISAXS, GID, RSM, MXD, etc) but opening new possibilities of sample environment (cryostats, magnetic fields) and techniques (Magnetic Diffraction, X-Ray Standing, surface diffraction, microdiffraction) due to the improvement in payload, flux and beamsize. The third SAGUI's experimental station (58m) will be based in the current XRD2 diffractometer, which will be dedicated to scattering and diffraction techniques in weighty sample environments, like the Langmuir trough or the spin-coating setups today available at XRD2. The source of SAGUI is planned to be a 19mm-Delta undulator, positioned at a low-beta strait section, which allows tuning of the polarization and gives a small ($20 \times 3 \mu m^2$) and collimated ($17 \times 12 \mu rad^2$) beam. The optics is based in a simplified version of the in-house developed vertical bounce HD-DCM (High Dynamics Double Crystal Monochromator) in which the long stroke movement, required to low energies is withdrawn. Positioned at approximately 28.5m from the source, it has two pairs of cryogenic cooled Silicon crystals – (111) and (311) – which can handle the high power from the undulator source with high mechanical stability. The focalization scheme is intended to preserve the undulator source characteristics but giving the necessary flexibility and stability to move the focal position from one station to the other. This is accomplished by using two side-bounce Rh-coated mirrors, the first one with sagittal focusing (30.4m) and the second with meridional focusing (32.1m), which allows to change the focal position from 42m to 58m only by changing its angle of incidence □. These two fixed figure mirrors have nominal incidence of □=2.5mrad to focus at 53m. Both face the same side of the optical hutch as one must increase (decrease) the sagittal (meridional) mirror angle of incidence to bring the focus closer to the source (1st station), and the opposite to bring the focal position far from the source (3rd station). This poster will detail this optical design which delivers a beam with tunable energy from 4.8keV to 24keV (from 22Ti K edge to 45Rh K edge) with an expected flux close to 1012ph/s/100mA focalized at 53m and ($30 \times 10 \mu m^2$) focal size with a divergence at ($50 \times 20 \mu rad^2$).

KEYWORDS: SAXS, XRD2, GISAXS, GID, RSM, MXD

ORAL PRESENTATION

TROJAN HORSE IN ZEOLITE SYNTHESIS: A XAS STUDY ON THE FIRST STRUCTURE-DIRECTING AGENT BASED ON AS CATIONS

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Zeolites are crystalline microporous materials, mainly constituted by silicon oxide where the Si atom can be isomorphically replaced by other elements (Al, B, Ga, Ti, Ge, Sn, etc). The well-defined size and distribution of the structural channels of each different zeolitic framework type together with the chemical composition confer to these materials multiple applications in processes such as gas adsorption and separation, catalysis and encapsulation or controlled release of molecules, among others, some of them with industrial applications. This is the driving force for studying novel methods for the preparation of novel zeolitic structures, since it would give the possibility of obtaining tailored materials with the most appropriate channel system for each specific application [1]. To obtain new structures, several approaches have been attempted, such as the incorporation of fluoride in the synthesis gel replacing the hydroxyl anions as silica-mobilizing agent or the isomorphic substitution of Si with Ge, which present a strong directing effect, favouring the formation of not only the D4R units but also the previously elusive double three membered-ring (D3R) units opening the doors to new families of zeolites. Nonetheless, the most important approach for obtaining new zeolites has been the use of different families of organic structure-directing agents (OSDAs) [3]. Expanding the previously known family of onium (ammonium, phosphonium and sulfonium) organic structure-directing agents for zeolite synthesis, a new member, the arsonium cations, is used for the first time and reported here. The new group of tetraalkylarsonium cations has allowed synthesizing the zeolite ZSM-5 with several different chemical compositions, opening a route for the synthesis of zeolites with new series of OSDA. Furthermore, the use of arsenic played an essential role in the study of the OSDA entrapped in the zeolite, as its higher electronic density respect to phosphorus, sulphur or nitrogen allowed its localization by powder X-ray diffraction, as well as the use of 75As MAS-NMR and XAS at the As K-edge to analyse the location and properties of the molecule. In this sense, the As atom can be considered as a Trojan Horse probe inside the OSDA molecule to enable for its study. Notwithstanding, the influence of trivalent elements such as B, Al or Ga isomorphically replacing Si atoms in the framework structure and their interaction with the As species has been studied.

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KEYWORDS: ZEOLITE, STRUCTURE-DIRECTING AGENT, ARSENIC, X-RAY ABSORPTION SPECTROSCOPY

ORAL PRESENTATION

ULTRA-HIGH CONDUCTIVE HOLLOW CHANNELS GUIDED BY BAMBOO BIO-TEMPLATE FOR ELECTRIC AND ELECTROCHEMICAL DEVICES

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The fabrication of well-aligned arrays of microfluidic channels is very challenging using conventional microfabrication processes. Nature is unique on creating complex hierarchical architectures, for instance, some wood-derived materials have aligned channels that offers the possibility to add new functions to biological templates, necessaries for green electronic, biological devices and energy applications.[1] In order to explore novel hierarchical architectures, biological structures have been used as bio-templates for the fabrication of functional biodevices. Understanding the complexity of living systems, its anisotropic structures, as well as incorporation of metal ions, metal-organic framework (MOF), conductive organic polymers and nanomaterials to increase or add new functionalities to plants, is important to promote plant science and bio-nanotechnology devices. Herein, in this work, we developed for the first time a room temperature fast prototyping method to fabricate ultrahigh conductive arrays of conductive microchannels using bamboo matrix as bio-template. Considering its lightweight and strengthened mechanical properties, bamboo as raw biomass is the best candidate to be explored as a lignocellulosic natural resource for a scalable production of eco-friendly, sustainable, low cost and portable electronic and electrochemical biodevices. Our method consists of flowing silver ink through the array of microchannels in bamboo Dendrocalamus Giganteus and removing the excess of ink by flowing nitrogen. We achieved a regioselective coating of the bamboo vascular bundles with a conductivity of 9.3 (± 4.0) × 10^5 S m^{-1} (□ǁ), which is the highest value reported so far for tracks along the vascular network of wood-derived materials. Moreover, the hollow conductive channels enabled the fabrication of unprecedented electronic and electrochemical bamboo-based devices that we call “bambootronic” technology. As a proof-of-concept we will present 3D electrical circuits, multi-channel microfluidic heater, and fully integrated carbon-based electrochemical cell using carbon black nanostructures. We would like to perform new experiments at Mogno Lab (MicrO and NanO Tomography) of the new LNLS/Sirius. To analyze the metal nano e microsized coating dispersion into lignocellulose microchannels we need the use a real time nondestructive technique. Our aim is to determine the selective region coated by metal nanoparticles and quantify the volume fraction of their aggregates after several cycles of injection and drying of colloidal solution with different chemically modified metal nanoparticles. Beside that we would like to experiment the possibility to observe higher contrast of empty array vessel when concentrated colloidal nanoparticles solutions are injected IN-SITU into the bamboo specimen. To deeply control the production of hybrid bio-engineering material, the bamboo filled system has to be fully characterized on the nano and microscale dimension to determine the following data: metal-polymer interaction inside the biological matrix, density aggregates per volume, the volume fraction of the cluster in to the microambient and the interfacial region between the metal coating and microchannels system. The filled bamboo with the selected metal nanoparticles can pave the way for new functional materials for new bambootronic generation system.

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KEYWORDS: BIO-DEVICE, ELECTROCHEMICAL CELL, MICROFLUIDIC HEATER, BAMBOOTRONIC

POSTER PRESENTATION

UNEXPECTED OPTICAL BLUE SHIFT IN LARGE COLLOIDAL QUANTUM DOTS ELUCIDATED BY XAS

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Semiconductor Nanocrystals (NCs) are the focus of very active research in the quest for materials with tunable optical and electronic properties.[1,2] Despite their current use in nowadays technology including new screen TV (QLED) or lamps acting as energy-efficient light sources, they are still the motivation of numerous fundamental physico-chemical studies.[1,3] Among them, multinary NCs (tertiary or quaternary in composition) are gaining interest in solar power conversion and biological in vivo imaging applications, where longer wavelengths are demanded.[4] Although a huge effort has been performed by the scientific community to dominate particle size, shape, composition and crystallinity, the diversity of synthetic procedures and suitable chemical precursors have led to a broad variety of NCs. In this sense, we had initiated a systematic work on the study of the synthesis and characterization of quaternary CdSeZnS quantum dots. In first place we study an alternative approach to grow inorganic shells on CdSe NCs, which implies the removal of the original long insulating ligands to a large extent, simultaneously with the fabrication of core–shell structures under friendly working conditions (room temperature and ambient atmosphere). In the next step, the compositional changes taking place during the synthesis of alloyed CdSeZnS nanocrystals are studied. While size and composition are the two main factors affecting the optical properties, the spatial distribution of the elements and the nature of the interfaces between the different regions composing the NCs also influence the final optical response. In this case, the traditional red shift concomitant to the increasing NCs' size competes with compositional changes taking place during the reaction. The upshot of this competition is mainly controlled by temperature, which defines the evolution of the NCs' structures and optical properties. Notably, in this work, the changes in composition, responsible for the intriguing blue-shifted optical response as the NCs grow larger, have been elucidated through X-Ray Absorption Spectroscopy (XAS) measurements at the L3-Cd, K-Se, K-Zn and K-S edges. The results are understood in the frame of ion exchange and migration mechanisms taking place not after post-treatments but IN-SITU during the synthesis of the NCs, which provides an extra degree of freedom and increases the versatility of the hot injection method. Further, it demonstrates an additional route to tune the composition of QDs and to modulate the emission wavelength through band gap engineering.

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KEYWORDS: QUANTUM DOTS, CDSEZNS, CORE/SHELL, XAS

POSTER PRESENTATION

VUV PHOTOIONIZATION AND IONIC DISSOCIATION DYNAMICS OF THE 2-AZETIDINONE MOLECULE

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Introduction: The 2-azetidinone (C_3H_5NO) molecule belongs to the group of organic compounds called heterocycles, which are present in the formulation of important complex chemical entities, such as carbohydrates, proteins, among others, and stand out for their diverse properties and applications important to several fields. The main goal in this project is to provide reliable fundamental spectroscopic and spectrometric data for this group of molecules in gas phase by using synchrotron radiation, photoelectron photoion coincidence and time of flight mass spectrometry techniques. Methods: TOF-MS and photoelectron photoion coincidence (PEPICO) techniques have been employed. VUV synchrotron radiation sources was employed as electronic excitation and photoionization agent, from the TGM beamline at the LNLS-CNPEM facility. Total and partial ion yields (TIY,PIY) and PEPICO spectra were recorded as a function of the incident photon energy, covering from the valence region up to 21.5 eV. The resulting photoionization ion products and the possible fragmentation pathways leading to those species are presented and discussed. We have also performed quantum chemical ab initio calculations at several theory levels in order to obtain structural and energetics parameters for this molecule and ion products, in order to combine with the experimental data for a better understanding of this molecule and its behavior upon VUV photoionization. Results: The valence photodissociation studies of 2-azetidinone, the PEPICO mass spectra have been recorded covering the range from 9 eV to 21.5 eV. The first ionization energy occurs at about 9.7 eV. The high photo-stability of this molecule and its molecular parent ion has been confirmed from our results, as the molecular ion is the only photoionization product species present in the spectra up to 12eV, and still remains as an important species in the entire range of energies in this work. It has been mainly attributed to the strong bonding resulted from its compacted closed ring molecular structure. The dominant fragmentation mechanisms in this energy range corresponds mainly to the consecutive dissociations of the C-N and C-C bonds from the 2-azetidinone molecular ion resulting in three possible ion fragments with $m/z = 28$. The ion yield spectra were recorded by scanning the incident photon energies in the 9 - 21.5 eV showing the expected broad spectral features resulting from valence electronic excitation and ionization from the molecular ground state leading to the corresponding ionic states. In addition, the corresponding mass spectra based on the PEPICO technique recorded at selected photon energies in the valence region provided relevant information leading to the identification of the dissociative photoionization ion products, and their corresponding fragmentation pathways. Conclusions: Time of flight mass spectrometry (TOF-MS) used in conjunction with photoelectron photoion coincidence (PEPICO), total and partial ion yield (TIY and PIY) techniques, as well as quantum chemical ab initio calculations, have been proved powerfull tools for the analisys of the electronic structure and photodissociation dynamics of the 2-azetidinone molecule in gas phase, which resulted in very interesting chemical and physical insights.

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KEYWORDS: PHOTOIONIZATION, IONIC DISSOCIATION, SYNCHROTRON RADIATION, PEPICO, 2-AZETIDINONE

Poster Presentation

XANES STUDY OF CERIUM OXIDATION STATE OF CE-FE-O CATALYSTS IN CATALYTIC OPERATING CONDITIONS

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Ceria-based mixed oxides have been widely studied in the past years due to their redox properties. The presence of the Ce^{4+}/Ce^{3+} couple provides high oxygen storage capacity to these materials which can be further improved by the adition of aliovalent dopants to the CeO_2 fluorite structure. These properties are of great interest for catalytic and electrocatalytic applications. Therefore, the main objective of this work is to study the effect of temperature and fuel composition (H_2 or CH_4/CO_2) in the Ce^{3+}/Ce^{4+} ratio in Ce-Fe-O mixed oxides, which is strongly related with redox and catalytic performance of the samples. Ce-Fe-O mixed oxides were synthesized by cation complexation with citric acid, liquid mix and freeze-drying methods and fired at 500°C. The solids studied have the following compositions: $Ce_{1-x}Fe_xO_\delta$ with x = 0, 0.05; 0.10; 0.15, 0.20 and 1. Furthermore, some selected samples with superior catalytic and electrocatalytic performance at conventional laboratory experiments were fired at 800°C and impregnated with NiO (5%at. Ni). In-situ DXAS experiments were performed at the D06A-DXAS dispersive beam line of the LNLS in the energy region corresponding to the Ce LIII-edge. Temperature programmed reduction (TPR) experiments were carried out by heating the samples in a flow of diluted hydrogen, from room temperature to 800°C. Synthetic biogas conversion to syngas was studied in samples impregnated with NiO. From in-situ DXAS experiments we concluded that product distribution observed in mass spectrometer data was significantly correlated to Ce^{4+}/Ce^{3+} ratio in the samples during catalytic tests with CH_4/CO_2 feed flow. Sample $5Ni/Ce_{0.9}Fe_{0.1}O_\delta$ exhibited very intense H_2 and CO signals when a steep peak of Ce reduction was observed at 750°C. Afterwards Ce re-oxidation was observed followed by H_2O and CO_2 production. Sample $5Ni/Ce_{0.9}Fe_{0.15}O_\delta$ exhibited a less intense peak in Ce reduction and very small production of CO and H_2 whereas non-supported $Ce_{0.9}Fe_{0.1}O_\delta$ exhibited a continuous increase in Ce reduction and virtually no CO and H_2 production, reaching ca. 20% Ce reduction values in contrast to the 7.5% obtained for sample $5Ni/Ce_{0.9}Fe_{0.1}O_\delta$. This results can be correlated to our previous conventional laboratory tests where Sample $5Ni/Ce_{0.9}Fe_{0.1}O_\delta$ exhibited superior catalytic activity and stability in time-on-stream experiments. Therefore, samples that are more prone to exchange oxygen from the lattice during experiments with hydrocarbon feed appear to be more tolerant to carbon formation and subsequent deactivation.

Keywords: CeO_2, XANES, biogas

Poster Presentation

XAS STUDY ON THE INCORPORATION OF ARSENIC SPECIES IN CARBONATES MINERALS OF ARGENTINA

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Arsenic (As) contamination of surface and groundwater represents a serious environmental problem in many regions of Argentina. Geogenic As-contaminated waters are at equilibrium or slightly supersaturated with respect to calcite. This is the mechanism of formation of travertine rocks associated with carbonate and As-rich thermal waters in the Andean region. As rich carbonates also precipitate in soils of the Chaco-Pampean plain in the form of calcretes. As concentrations in the calcretes is ~10 ppm, while in travertines As concentrations are much higher (~3500 ppm). Regardless of their origin, these carbonates may play an important role in the mobility of As [1]. Several scientific contributions are focused on the capacity of natural calcite to retain As-oxyanions. In the last decades, it was demonstrated that As-oxyanions may adsorb onto calcite surface and/or substitute the carbonate group, in the calcite structure [2]. The aim of this study is to identify the As species in carbonates precpitated in different geologic environments associated with areas where high As concentrations have been reported in the water. X-ray absorption spectroscopy (XAS) was used to determine the oxidation state of As and their local chemical coordination. To carry out this study, three samples were analyzed: pedogenetic calcretes, geothermal and biogenic sediments were collected in the Chaco-Pampean and in the Puna region. XAS spectra were collected at the XAFS1 beamline at the Brazilian Synchrotron Light Laboratory (LNLS) in Campinas, Brazil. The XANES analysis allowed differentiating two oxidation states of As in the studied samples. As(V) is the dominant oxidation state (80-100%) while the As(III) represents less than 20% of the total As. EXAFS analysis indicate that As is mainly present in the form of As(V)-O species.Specifically, the proposed models resemble an arsenate-like structure, with the ~4 O atoms at a distance of ~1.68 Å around the As atom. The noisy EXAFS spetrum of the calcretes does not allow discriminating the second coordination shell; therefore, the obtained values can be adjusted to arsenate adsorbed onto either calcite or Fe(III)-(hydr)oxides. On the other hand, in geothermally and biogenically precipitated carbonates, the best EXAFS models suggest the presence of ~1 Fe atom at ~2.9 Å, ~2 Ca atoms at ~3.6 Å and ~2 Ca atoms at ~3.7 Å. The As-Fe shell is typical of arsenates adsorbed onto Fe(III)-(hydr)oxides, while the As-Ca shells are typical of arsenate substituting carbonate ions in the calcite structure.

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Keywords: As solid speciation, Calcretes, travertines

POSTER PRESENTATION

X-RAY DIFFRACTION CHARACTERIZATION OF MICRO/NANO-STRUCTURED PEROVSKITE OXIDES PREPARED BY EDTA/NH_4NO_3-NITRATES GEL COMBUSTION

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Perovskite oxides ABO_3 and related compounds are a vast and very flexible family of oxides [1]. They are, not only the broadest chemical sandbox but also a huge test bank for properties since they are known for a myriad of applications, notably piezoelectrics, superconductors, mixed ionic-electronic conductors, catalysts, etc. Additionally, perovskites play a key role in our current understanding of strongly correlated materials [2]. In the search for the simple preparation of nanostructured perovskite oxides for solid oxide fuel cell applications, we have adapted the gel-combustion method for a rapid one or two-step preparation of a wide variety of perovskites. The auto-combustion methods proceed with the dissolution of metallic precursors in a dissolution of EDTA (ethylenediaminetetraacetic acid - $C_{10}H_{16}N_2O_8$) and ammonium nitrate (NH_4NO_3) in a 1:1.1:n molar proportion at pH=10 (achieved by the addition of NH_4OH). The solvent is evaporated at 120°C until a dry paste is obtained. The paste is heated at 300-350°C where, NH_4NO_3 fusses and later decomposes, in controlled combustion that yields the final nanostructured perovskite, when this is the thermodynamically stable phases at the combustion temperature. This was observed for $LaMO_3$ with M=Cr, Mn, Fe, Co and mixed M with V and Cu, La_2CuO_4, $SrMO_{2.5}$ (M=Fe, Co) and n=6-10. Alternatively, when the desired phase is not formed in the combustion step, an amorphous precursor is obtained by reducing n in the initial solution. This solid is later fired in air to yield the desired perovskite, as observed in $(La,Sr,Ba)(Fe,Cu)O_{3-\delta}$ and $LnBa_2Cu_3O_{7-\delta}$ Ln=lanthanoid) compounds. The phases obtained from the direct combustion procedure, in batches of up to ~5 g in a short time of fewer than 4 hours, show an oxygen-reduced form, as confirmed by Xray diffraction and thermogravimetric experiments, that has not been previously reported. The phases obtained in the two-step procedure show normal oxygen content but could be obtained in ~10 g amounts in less than 24 hours. In this presentation, we will show the systematic study of simple, double, layered and Ruddlesden-Popper perovskites by X-ray powder diffraction data collected at D10B-XPD beamline of LNLS, successfully prepared by this method.

KEYWORDS: PEROVSKITE, NANO/MICROSTRUCTURED, X-RAY POWDER DIFFRACTION

POSTER PRESENTATION

X-RAY FLUORESCENSE MICROTOMOGRAPHY FOR IMAGING 3D ELEMENTAL CHARACTERIZATION OF CHITINIZED STRUCTURES OF *RHODNIUS PROLIXUS* : AN EVALUATION OF TRIFLUMUROM AS POTENTIAL TOOL FOR INTEGRATED VECTOR CONTROL PROGRAMS

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In this work, we report on the particular advantages of XRF tomography, using the XRF beamline at LNLS (Brazilian Synchrotron Light Laboratory), in the study of the biological effects of treatments with triflumuron (TFM) (Starycide® sc 480 Bayer) on the fifth instar nymph of *Rhodnius prolixus* , the most important insect vector of Chagas' disease [1]. Several works suggest that Triflumuron (TFM), represents a potential tool for the control of disease vectors in public health. The main purpose of this work was to investigate possible changes in 3D elemental distribution within the exoskeleton of R. prolixus treated with TFM. Fifteen specimens of fifth-instar nymphs of *Rhodnius prolixus* were taken from the Laboratory of Biochemistry and Physiology of Insects, Oswaldo Cruz Foundation (FIOCRUZ), Brazil, and were divided in two groups. In the first group, immediately after feeding the insects with defibrinated rabbit blood, a Starycide® containing 48 g of TFM per 100 mL, provided by Bayer (Brazil), was applied directly to the ventral surface of the abdomen of these insects [2]. The second group, the control group, remained also unfed and was kept under the same conditions. They were sacrificed after 25 days. These two groups were compared using XRF tomography. We investigated chemical effects of treatments with Triflumurom in *Rhodnius prolixus* by producing three-dimensional maps of the distribution of individual elements such as Ca, Cu, Fe and Zn. The maps obtained showed significant differences between treated and control groups. These results can help to evaluate the efficacy of the growth regulator, TFM, for disrupting the development of R. prolixus fifth-instar by topical treatment. With the new 4th generation light source (SIRIUS) we expect to continue this project at the Carnaúba beamline, using an experimental station dedicated to X-ray Fluorescence Tomography in the hard X-rays energy range (5 to 20 keV).

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KEYWORDS: X-RAY FLUORESCENSE MICROTOMOGRAPHY, *RHODNIUS PROLIXUS* , TRIFLUMUROM

ORAL PRESENTATION

X-RAY SPECTROSCOPY FOSTERING THE UNDERSTANDING OF FOLIAR UPTAKE AND TRANSPORT OF MN BY SOYBEAN (GLYCINE MAX L. MERRIL): KINETICS, CHEMICAL SPECIATION AND EFFECTS OF GLYPHOSATE

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Soybean is the main source of protein used for livestock feeding, and despite recent controversies, glyphosate is a factor that contributes to increase soybean productivity. However, glyphosate can interfere on spray mixture stability and on the metabolism of micronutrients. Using in vivo X-ray spectroscopy and scanning electron microscopy, we investigated the effects of glyphosate on soybean foliar uptake and transport of manganese, provided by $MnSO_4$, $MnHPO_3$, Mn-EDTA and $MnCO_3$. The fertilizer solutions induced damages to the leaf epidermis, regardless the glyphosate mixture. Glyphosate decreased Mn uptake and transport from $MnSO_4$, $MnHPO_3$, and $MnCO_3$ sources. It seems that it complexes Mn yielding a solid deposited on the leaf surface. We did not find evidence of Mn-glyphosate complexation within the plant, it was rather transported in the same chemical environment regardless the source and the presence of glyphosate, except for Mn-EDTA. For this latter source, Mn was absorbed and transported in its pristine form. Interference of glyphosate on nutrition of soybean seems more related to complexation on tank mixture rather than affecting the internal metabolism of nutrients.

KEYWORDS: GLYCINE MAX, MANGANESE, GLYPHOSATE, FOLIAR UPTAKE, XRF, XANES, SEM

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