CATERETÊ WORKSHOP

4TH INTERNATIONAL USER WORKSHOP ON COHERENT X-RAY IMAGING AND SMALL ANGLE X-RAY SCATTERING

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FOREWORD

It is a great pleasure to host the "**4th International User Workshop on Coherent X-ray Imaging and Small Angle X-ray Scattering**" (Cateretê Workshop 2020) at the brand-new building of Sirius.

Promoted by the Brazilian Synchrotron Light Laboratory (LNLS/CNPEM), funded by CAPES and sponsored by Anton-Paar, this two-days event aims to present and discuss the new scientific perspectives offered at the coherent scattering beamline, Cateretê, specifically, X-ray imaging and time-resolved capabilities.

When coming into operation, it will provide cutting edge research tools that are non-existent today in Brazil, such as 3D imaging (CDI) with 10's nanometer resolution, X-ray photon correlation spectroscopy (XPCS) to study dynamics and ultra-small angle X-ray scattering (USAXS).

In the 2020 edition, the event will comprise research results and experiment perspectives organized in invited talks, oral communications and poster presentations from students and scientists coming from different parts of Brazil and South America.

During the event, the participants will have the opportunity to visit Sirius and Cateretê beamline and to discuss project and experiment possibilities with experienced scientists.

We wish all a nice and productive workshop!

Scientific and Local Committees.

ABSTRACTS

ANISOTROPIC RECRYSTALLIZATION OF PCL/SBA-15 COMPOSITES DURING 3D PRINTING: A SAXS STUDY OF THE INFLUENCE OF PROCESSING PARAMETERS

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Additive manufacturing represents nowadays one of the most disruptive technologies, both in academic and industrial fields. In this context, the design and 3D printing of biomimetic materials for tissue engineering and regenerative medicine applications have attracted a lot of attention. However, a key step that must be overcome in order to design and fabricate new functional materials is to have a better understanding about the effect of some process parameters on the final structure of materials. Recent works showed some interest in this area, and have investigated the structural evolution of PCL during 3D printing and the effect of particle alignment induced by extrusion-based 3D printing on final structural properties of 3D printed materials [1,2]. In the present work, mesoporous silica particles (SBA-15) were incorporated into a polycaprolactone (PCL) matrix through an extrusion-based process, to obtain a filament compatible with melt extrusion-based 3D printing systems. In order to study the effect of processing parameters and particle alignment on the polymer recrystallization, PCL and PCL/SBA-15 samples were printed using two different nozzle sizes, 0.25 mm and 0.40 mm. Structural characterization of PCL and PCL/SBA-15 3D-printed samples was performed by small-angle X-ray scattering (SAXS). Measurements were carried out using a Xeuss 2.0 (Xenocs, France) with a sample-to-detector distance of 1200 mm and $\lambda = 0.154$ nm which allowed us to study both the lamellar structure of PCL and the hexagonal pore structure of SBA-15. Analysis of 2D SAXS patterns showed that rod-like SBA-15 particles were aligned along the print direction, as expected. More interestingly, PCL presented anisotropic recrystallization, perpendicular to the print direction only in the presence of SBA-15 (anisotropic patterns were not observed when PCL samples were studied). Results indicate that melt extrusion-based 3D printing aligns high aspect ratio SBA-15 particles, which induces anisotropic recrystallization of PCL, and the alignment is dependent, for instance, on the nozzle size. To have a better understanding of the influence of processing parameters on the recrystallization and orientation of polymer crystals, we propose the use of CATERETÊ beamline at Sirius, in particular, the X-Ray Photon Correlation Spectroscopy (XPCS) facility. Since XPCS has proved to be an excellent technique to study polymer dynamics [3], we consider that this technique would shed some light on the anisotropic recrystallization of polymers in the presence of anisotropic particles.

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CATALYTIC PROPERTIES AND LOCAL STRUCTURE STUDIES OF ZINC SPINEL FERRITE NANOPARTICLES

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Zinc spinel ferrites, ZnFe2O4, were prepared by co-precipitation method, annealed at 420 ºC, and characterized by X-ray diffraction, X-ray absorption and 57Fe Mössbauer spectroscopies. The effect of Fe+3 rearrangement between the two preexisting octahedral and tetrahedral sites in their catalytic properties was investigated in this work. It was shown that the Zn doping lead to an increase of spinel ferrites lattice parameters as well as an improvement of their catalytic behavior towards the degradation of indigo carmine compared to undoped sample. It was observed that in the photo-Fenton process the indigo carmine concentration decreased to 98% of its initial concentration after 240 min of reaction.

CHALLENGE PROPOSAL FOR THE CATERETÊ BEAMLINE FROM THE SOFT MATTER LABORATORY

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Gel and gel-like materials have very attractive basic and applied properties and display a wide range of applications in medical, cosmetics, and food industry. From a very basic point of view, once a material has overcome the percolation threshold, its properties change dramatically and several “single molecule” properties become apparent. Gels have two main spatial scales associated with specific gel characteristics: (i) local fluctuations around entanglements (1-10 nm, almost independent of crosslinking density) and pore and cavities (100 nm to microns, dependent on crosslinking density). Moreover, gel dynamics is characterized by relaxations in the Hz-kHz range, especially suited for XPCS experiments. This kind of relaxation are of paramount importance during particle/molecule diffusion across the gel. Furthermore, micrometer and millisecond scaled phenomena in gels are strongly influenced by mechanical perturbations in Hz to kHz scale making the rheology-XPCS coupling an attractive experimental alternative. Even more, the design parameters of the beamline should allow the possibility to investigate the dynamics of x-ray reflectivity opening the possibility to investigate interfacial dynamics. As specific examples, our interest focuses on: -USAXS/SAXS/XPCS in chemically and physically cross-linked gels. Expected output: relevant size and time scales under different chemical and physical conditions. -Nanoparticle dynamics and diffusion inside gels. Expected output: particle dynamics under different mechanical efforts (rheology coupled). -Interfacial structure (XRR/GIXOS) and photon correlated-XRR. Expected output: interfacial dynamics at different length scales. 2) Metal organic frameworks (MOFs) are porous crystalline materials formed by metallic nodes (usually transition metals ions) and organic linkers. Owing to their large surface area and porosity and high content of metal ions, MOF-based nanoparticles are been applied in diverse fields including catalysis, drug delivery, pollutant adsorption. In this context, and considering our previous experience on MOFs, our interest focuses on: -Studying the internal structure changes by CDI on MOFs nanoparticles (based on MOF structures like MIL-101, HKUST-1, ZIF-8, and derivatives) at a single particle level and in operando conditions during relevant catalytic reactions (like CO2 reduction, or organic molecule oxidation) -Assessing the formation and metallic ion distribution during the formation of bimetallic MOF nanoparticles (like ZIF-8/67) by ASAXS and CDI. 3) The application of nanomaterials for treating and diagnosing diseases (nanomedicine) has experimented and exponential grow in the last years. One of the main challenges that this field face, is to understand the complex interactions that nanoparticles experiments when in biological media. In particular, the adsorption of proteins and the formation of the so-called “protein corona” completely change the biological fate of nanomaterials owing to the modification of surface properties. Considering this, our interest focuses on: -Following the kinetics of protein adsorption using ultra-fast SAXS/WAXS measurements and determining the structure of the adsorbed protein shell. In this sense, we would like to answer (using SAXS and cryo-TEM) whether the adsorbed shell is homogenous, or some protein clustering occurs owing to surface properties or experimental conditions (e.g. tradition titration schemes vs. microfluidic set-ups). -Obtaining basic information on protein conformation (alpha helices, beta-sheets) by WAXS during adsorption. In addition, getting information on the motility of proteins over nanoparticle surface by XPCS.

CHARACTERIZATON OF ORDERED MESOPOROUS SILICA AND VACCINE ANATOXINS FOR ORAL IMMUNIZATION APPLICATIONS

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Using nonionic surfactants of high molecular weight (triblock copolymer Pluronic P123 (PEO20PPO70PEO20) in acidic aqueous medium, Zhao et al. [1] obtained highly ordered mesoporous silica (OMS), named SBA-15, which have the capacity to release and adsorb molecules inside its pores. This kind of material has many applications in several areas such as petroleum refining industry, catalysis and microelectronics, but also in the medical field, with the encapsulation of drugs such as anti-inflammatory ibuprofen [2] and camptothecin and immobilization of globular enzymes [3], for instance. In the field of immunology, Mercuri et al. [4] and Carvalho et al. [5] demonstrated that the SBA-15 acts as an efficient adjuvant, along its protective effect, crucial do maintain the antigen immunogenicity in the hostile stomach environment [4]. For the later application, the comprehension about protein encapsulation process is fundamental, and it depends on the knowledge about the individual species SBA-15 and antigens, which is the focus of this work. We firstly investigate the protein structure of Diphteria and Tetanus toxoids (DTd and TTd) using small-angle x-ray scattering (SAXS). They are produced by the chemical detoxification of the respective native toxins through formaldehyde treatment [6], and are supplied by Butantan Institute (São Paulo, Brazil). From literature, it is expected that DTd and TTd have molecular weights of ~60 and ~150 kDa, with maximum size ~9 and ~15 nm, respectively [7]. Because of the larger size of TTd compared to SBA-15 mesopores diameter (~10 nm), we will also investigate, by SAXS and nitrogen adsorption isotherm (NAI), the expansion of the pores using the swelling agent 1,3,5-triisopropylbenzene (TIPB), added to the initial stage of the silica synthesis [8]. In this context, additional dynamic light scattering (DLS) will provide useful information about the aggregation state of the proteins in order to enable their future encapsulation into SBA-15 mesopores.

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COMBINED MAGNETOLIPOSOME FORMATION AND REMOTE CONTROLLED DRUG RELEASE

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This work is focused on the synthesis of magnetoliposomes with controlled size, study on the effect of different nanoparticle spatial distribution, in its membrane integrity, along with their colloidal, magnetic and heating properties. We have evaluated the use of these magnetoliposomes as drug delivery carriers using doxorubicin applied to MDA-MB-231 and HeLa cells. We have analyzed cellular uptake of magnetoliposomes and their therapeutic effect when loaded with doxorubicin by studying cell viability and proliferation. We have also studied the controlled mechanism for drug release on demand using an external alternate magnetic field. The Caterete synchrotron beamline will be used in the future to generate images of magnetoliposome structures for understanding interactions between magnetic nanoparticles and lipids. Also cells derived from BCPAP human papillary carcinoma with magnetoliposomes will be used for verification of the in-vitro localization of this material.

ENVIRONMENTAL TOXICOLOGY RESEARCH OF MICRO AND NANOPLASTICS USING ADVANCED TECHNIQUES AT CATERETE BEAMLINE OF SIRIUS

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Environmental toxicology studies the fate and the damage of pollutants in the human health and the ecosystems. As a result of global plastic production and consumption practices, micro and nanoplastics (MNPs) are emerging contaminants in both aquatic and terrestrial environments. Nowadays, public concerns about MNPs have increased due to the possible adverse effects on biological and environmental systems and the consequences on human health [1]. Synchrotron-based methods are being used progressively in many areas of environmental toxicology research. The new Brazilian synchrotron radiation source, Sirius represents today one of the most modern synchrotron sources capable of studying several kinds of materials with unprecedent brilliance [2]. Cateretê (Coherent And TimE REsolved scatTEring) is a beamline optimized to perform Coherent X-ray Diffraction Imaging (CXDI) and X-ray Photon Correlation Spectroscopy (XPCS). This beamline will operate from the tender X-rays, 3 keV up to 12 keV, for imaging of biological and nanomaterials, making the most of the coherence properties of the radiation provided by Sirius. The sample environment is under commissioning and will enable to perform 3D-CDI, ptychography, Bragg CDI and XPCS measurements. It will be equipped with an interferometry system, a cryogenic device for biological specimens and catalytic reactors for in situ studies [2]. The potential toxicity of MNPs to aquatic organisms is a matter of interest since the increase of commercialization and disposal will inevitably lead to some instances of inadvertent environmental exposures. Guidelines for the ecological toxicity testing of MNPs were identified as a priority goal by the OECD [3]. For that purpose, we propose the previous characterization of selected MNPs at CEPROCOR and UNC, and the development of ecological studies using the innovative facilities of LNNano. Furthermore, we also aim the use of advanced techniques at CATERETE beamline of Sirius that would provide a powerful mean for characterizing the toxic, biological and environmental behaviors of MNPs enabling new perspectives for research in strategic areas such as environmental toxicology, life sciences, nanotechnology and many others. As the technology improves and more facilities of synchrotron light sources and efficient beamlines are developed, a significant transformation is taking place in the field of environmental toxicology, since researchers can now take advantage of these new techniques to collect data in ways that have previously not been possible.

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Keywords: Synchrotron radiation; environmental toxicology, micro(nano)plastics, CATERETE, Sirius.

FISIK: FRAMEWORK FOR THE INFERENCE OF IN SITU INTERACTION KINETICS FROM SINGLE-MOLECULE IMAGING DATA

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Recent experimental and computational developments have been pushing the limits of live-cell single-molecule imaging, enabling the monitoring of intermolecular interactions in their native environment with high spatiotemporal resolution. However, interactions are captured only for the labeled subset of molecules, which tends to be a small fraction. As a result, it has remained a challenge to calculate molecular interaction kinetics, in particular association rates, from live-cell single-molecule tracking data. To overcome this challenge, we developed a mathematical modeling-based Framework for the Inference of in Situ Interaction Kinetics (FISIK) from single-molecule imaging data with substoichiometric labeling. FISIK consists of (I) devising a mathematical model of molecular movement and interactions, mimicking the biological system and data-acquisition setup, and (II) estimating the unknown model parameters, including molecular association and dissociation rates, by fitting the model to experimental single-molecule data. Due to the stochastic nature of the model and data, we adapted the method of indirect inference for model calibration. We validated FISIK using a series of tests in which we simulated trajectories of diffusing molecules that interact with each other, considering a wide range of model parameters, and including resolution limitations, tracking errors, and mismatches between the model and the biological system it mimics. We found that FISIK has the sensitivity to determine association and dissociation rates, with accuracy and precision depending on the labeled fraction of molecules and the extent of molecule tracking errors. For cases where the labeled fraction is too low (e.g., to afford accurate tracking), combining dynamic but sparse single-molecule imaging data with almost-whole population oligomer distribution data improves FISIK's performance. All in all, FISIK is a promising approach for the derivation of molecular interaction kinetics in their native environment from single-molecule imaging data with substoichiometric labeling.

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HYBRID CROSSLINKING TO IMPROVE HYDROGEL TOUGHNESS FOR TISSUE ENGINEERING: IN SITU SAXS STUDY UNDER TENSILE LOADING

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Because hydrogels exhibit similar properties to living tissues, they are interesting for biomedical applications but their brittleness limits their application range. Hybrid crosslinked hydrogels containing physical and chemical crosslinkers have shown improved toughness and elasticity. In this project, two hydrogels composed of poly(acrylic acid) (PAA) are polymerized in the presence of a network of Pluronic F127 micelles that act as physical crosslinkers. In the hybrid hydrogel, PAA is chemically cross-linked, whereas PAA is not chemically crosslinked in the physical hydrogel. SAXS patterns exhibit Bragg diffraction peaks characteristic of a face-centered cubic phase of F127 micelles, thus the ordered structure is maintained during PAA polymerization. The higher decrease of the lattice parameter observed in the hybrid hydrogel is accounted by greater network shrinkage provoked by the chemical crosslinker. Whereas pure chemically crosslinked PAA is brittle, the presence of micelles results in flexible materials. The ultimate tensile strength of the hybrid hydrogel is 2.5 times higher than the one of the physical gel but the chemical crosslinker limits its stretchability (elongation at break 290 % and 400 % in the hybrid and physical hydrogels). Energy-dissipation of the hydrogels was investigated by cyclic loading-unloading tests. The dissipated energy rises with strain and is higher in the hybrid gel, suggesting that higher damages occur. SAXS patterns were obtained while simultaneously deforming the hydrogels. The 2D patterns showed that the samples are initially isotropic but become anisotropic at 30 % of strain. Changes in intermicellar distance are observed during stretching, but this effect is restricted in the presence of a chemical crosslinker. Twelve hours after stretching, the hybrid hydrogel recovered its initial morphology whereas the physical one remained partially deformed. This set of results highlights that the presence of micellar physical crosslinks contributes to the stretchability of the sample and the chemical crosslinker hastens the recovery after deformation.

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INSITU INVESTIGATION OF STRUCTURE FACTOR EFFECTS BY SMALL-ANGLE X-RAY SCATTERING AND ACOUSTIC LEVITATION

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Particle interactions plays a very important hole on the system structure and the correlation between the nanoscale and macroscale properties of the investigated material. Scattering methods are well suitable for structural investigations in these cases since one can obtain direct information on the particle shapes, sizes, polydispersity and its interactions with the solvent and other particles in the system. Such information can be retrieved by the so-called form factors and structure factors [1]. For particles in solution, it is well known that the increase of the volume fraction of the solute decreases the average distance among the particles which, on the other hand, can induce the increase of the inter-particle interactions. The increase of volume fraction can be reached by the addition of more solute or by the removal of the solvent. The first approach can be obtained by a concentration series investigation or by the use of stopped flow methods. The latter option is much more difficult to be implemented in an usual way, since the removal of solvent is a not trivial procedure. In this work, an interesting application of acoustic levitation [2,3] and SAXS investigations what allows an in situ investigation of water based samples. As will be shown, the levitated drop naturally evaporates during the measurements, decreasing the solvent content and increasing the sample concentration. Therefore, one can investigate the increase of structure factor effects in real time.

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LIGNOCELLULOSE-BASED BIOTEMPLATE FROM BAMBOO BIOMASS FOR CHEMICAL, ELECTRIC AND ELECTROCHEMICAL BIODEVICES

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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 greener electronic, biological devices and energy applications. In order to explore novel hierarchical architectures, biological structures have been used as bio-templates for the fabrication of functional greener 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 single-walled carbon nanotubes (SWNTs) 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 catalytic and 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 chemical, electronic and electrochemical biodevices. Our method consists of flowing copper ions solution and silver ink through the array of microchannels in bamboo Dendrocalamus Giganteus. The fabrication of a new copper-functionalized lignocellulosic microreactor (Cu-LμR) from bamboo culms will be described together with its operation to perform a copper(I)-catalyzed 1,3-dipolar cycloaddition between azide and terminal alkyne (CuAAC). The bio-microfluidic device showed an easy prototyping and fast functionalization with copper ions. All reactions were carried out in flow regime with aqueous-methanol solvent and minimal leaching of copper, yielding a series of model 1,4-disubstitued triazole derivatives with good efficiency in a low-resource setting. With a regioselective metal deposition coating onto a bamboo vascular bundles we achieved a conductivity of 9.3 (± 4.0) × 105 S m-1 (□Ⅱ), 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 Cateretê beam line 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 ions and 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. 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.

LIQUID-LIQUID PHASE SEPARATION OF THE PRION PROTEIN MODULATED BY NUCLEIC ACIDS

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Misfolded prion protein (PrP) is related to Transmissible Spongiform Encephalopathies (TSEs). It was previously described that varied nucleic acids (NAs) can induce misfolding of native PrP leading to a conformation similar to the infectious form, the PrP scrapie. Here, we asked whether PrP undergoes liquid-liquid phase separation (LLPS) and if this process is modulated by nucleic acids. Interaction of recombinant murine prion protein (both full-length, rPrP23-231, and the globular domain, rPrP90-231) with different DNA sequences (25-mer DNA aptamers selected against PrP by SELEX and 21-mer double-stranded DNA sequences) was verified by isothermal titration calorimetry and fluorescence anisotropy. The structure of the aptamers was characterized by theoretical predictions, CD, NMR and SAXS. Aptamer binding caused dynamic aggregation of both constructions of the prion protein, resulting from the ability of PrP to undergo LLPS, as observed by SAXS, light scattering, DIC and transmission electron microscopies. While the free PrP globular domain phase separated into large droplets, aptamer binding increased the number of smaller condensates. Strikingly, a non-hairpin DNA induced transition to an ordered state, indicating amyloid formation on the droplets surface. In conclusion, we observed that PrP:NA interaction leads to LLPS and that this effect is modulated depending on NA structure and binding stoichiometry, shedding light on the role of NAs in PrP misfolding and TSEs.

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NANOSTRUCTURED CHARCOAL PRODUCTION FOR ADDITION TO POLYESTER BIOCOMPOSITES

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There is a tendency to increase the use of materials that, besides being low cost, may be environmentally friendly. The objective this research project was to evaluate the mechanical, physical, chemical and thermal properties of charcoal, relating them to the requirements for use in biocomposites. The wood properties of basic density, chemical composition, ash content and porosity were determined. Three pyrolysis temperatures were performed, 400°C, 600°C and 800°C, gravimetric yields, mass loss and volume loss and immediate chemical analysis of the charcoal were calculated. Thermogravimetric analyzes and confocal microscopy of the charred materials were performed. The most outstanding material for nanoscale transformation and addition in biocomposites, due to its high fixed carbon content, high density and higher thermal resistance, was charcoal produced in pyrolysis at 800°C.

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NOVEL PROCEDURE FOR DETERMINATION OF THE MELTING TEMPERATURE OF SPHERICAL NANOPARTICLES IN DILUTE SOLUTION AS A FUNCTION OF THEIR RADIUS BY EXCLUSIVELY USING THE SAXS TECHNIQUE

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The purpose of this investigation is to determine the melting temperature as a function of radius for dilute sets of spherical nanocrystals with wide radius distributions by a novel procedure exclusively using results of SAXS measurements. This procedure is based on the sensitivity of the SAXS function to small and rather sharp variations in size and electron density of nanocrystals at their melting temperature. The input for this procedure is a set of experimental SAXS intensity functions for varying temperatures. In practice, the sample is heated from a minimum temperature lower than the melting temperature of the smallest nanocrystals up to a temperature higher than the melting temperature of the largest nanocrystals. The SAXS intensity is recorded in situ at different temperatures along the whole heating process. This novel procedure was applied to three samples composed of dilute sets of spherical Bi nanocrystals with wide radius distributions embedded in a sodium-borate glass. The temperature versus radius function determined for Bi nanocrystals by using the method proposed here agrees very well with those reported in previous experimental studies using other methods. Our results also evidence the predicted size-dependent contraction of Bi nanocrystals induced by differences in surface-to-volume ratio of small nanocrystals and an additional size-independent compressive stress caused by the solid glass matrix in which liquid Bi nanodroplets are initially formed. This last effect is a consequence of the increase in the volume of Bi nanoparticles upon crystallization and also to differences in the thermal expansion coefficients of the crystalline phase of Bi and glass matrix. This additional stress leads to a depression of about 10 K in the melting temperature of the Bi nanocrystals confined in the glass. The procedure described here also allowed us to determine the specific masses and thermal expansion coefficients of Bi nanoparticles in both, liquid and crystalline, phases.

SAXS ANALYSIS TO DISCOVER THE IMPORTANCE OF GROWTH PARAMETERS OF COPPER ANTIMONY SULFIDE NANOPARTICLES

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Semiconductor nanoparticles have been applied in several technologies, such as solar cells, sensors, biological labels, and light emitting devices.[1] A major concern involving those materials is the use of toxic or scarce elements, especially lead, cadmium, and indium in their fabrication.[2] In this sense, semiconductor nanocrystal research have been moving toward earth-abundant and less toxic compounds. Our work deals with the growth dynamics of copper antimony sulfide nanoparticles. We followed the hot injection synthesis protocol, adding 0.45 mmol of CuCl, 0.45 mmol of SbCl3, and 7 mL of oleylamine in a three neck flask. The resultant mixture was degassed under vacuum at 80 °C and heated, under nitrogen atmosphere, to the reaction temperature (200 to 250 °C). In a separate flask, we added 1 mmol of sulfur in 3 mL of oleylamine and heated it to 60 °C, under vigorous stirring, 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, transmission electron microscopy, and small angle X-ray scattering (SAXS). The analysis of the X-ray diffraction patterns and the Raman spectra showed the formation of famatinite phase (Cu3SbS4) and chalcostibite phase (CuSbS2) in all the studied temperatures. In all temperatures, it was observed the formation of Cu3SbS4 after one minute of reaction and its transformation to CuSbS2. The transformation is found to be temperature dependent: it ocurred between 5 and 10 minutes in lower temperatures, such as 200 °C, while it happened between 1 and 2 minutes in higher temperatures, like 240 and 250 °C. To confirm this transformation, an experiment was designed, where the Cu3SbS4 nanoparticles were used as precursor, alongside oleylamine and SbCl3 at 200 °C. 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. The sample was characterized by XRD, indicating the presence of CuSbS2, confirming the sugestion of conversion from Cu3SbS4 to CuSbS2. The size evolution of the nanoparticles was followed by TEM and SAXS. The samples were diluted in hexane and the SAXS measurements were performed in a mica windowed sample holder. The SAXS data obtained were treated in the SASfit software package. The objective is to determine if the Cu3SbS4-CuSbS2 conversion is caused by a dissolution of the Cu3SbS4 and reassemble into CuSbS2 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. Acknowledgements The authors thank to CAPES and CNPq for financial support, CMM and CNANO/UFRGS. This research used resources of the Brazilian Synchrotron Light Laboratory (LNLS), an open national facility operated by the Brazilian Centre for Research in Energy and Materials (CNPEM) for the Brazilian Ministry for Science, Technology, Innovations and Communications (MCTIC). The SAXS1 beamline staff is acknowledged for the assistance during the experiments.

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SMALL- AND WIDE-ANGLE X-RAY SCATTERING - A VALUABLE TOOL FOR ANALYZING NANOSTRUCTURED MATERIALS USING A COMPACT LABORATORY SYSTEM

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The small- and wide-angle X-ray scattering (SAXS and WAXS) method draws increasing attention in the characterization of nanostructured materials. SAXS determines the size, shape and internal structure of colloidal structures in a range from typically 1 nm and 300 nm. Materials that can be analyzed include nanoparticles, surfactants, emulsions, liquid crystals, porous media, polymers and fibers. Nanostructured thin-film samples are analyzed using the GI (grazing-incidence) SAXS in which the X-ray beam penetrates the sample under a very shallow angle and retrieves information on the nanostructure only from surface and surface-near areas. WAXS ideally complements results obtained by SAXS since it provides essential information on a sample's crystallinity at the atomic level. For example, WAXS straightforwardly determines if a sample is monomorphic or contains polymorphic phases; the sample's crystalline structure can often be directly related to its properties like melting point, taste, etc. Both methods, (GI-)SAXS and WAXS, are ideally suited to analyze samples under changing external conditions, e.g. in-situ monitoring of processes in dependence of temperature, pH, additives, humidity, pressure, tensile stress, rheological shear, etc. In this contribution we will discuss selected applications of the SAXS/WAXS/GISAXS technique for characterizing different nanostructured materials, including dispersions of very large silica nanoparticles, BioSAXS studies of proteins in solution, GISAXS characterization of nanosized thin film samples and combined rheological-scattering measurements. All measurements were performed with the SAXSpoint 2.0 system, the most compact and versatile laboratory SAXS/WAXS/GISAXS system.

STRUCTURAL INVESTIGATION OF THE GROWTH MECHANISM OF SILVER NANOPARTICLE SYSTEM

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Metallic nanoparticles have been extensively investigated due their unique structural, optical and magnetic properties. The knowledge of the synthesis and growth processes of these systems is crucial to obtain nanoparticles with characteristics suitable for the intended application. In this work, we investigated the growth and nucleation process of silver nanoparticles during the synthesis process using “Small Angle X-Rays Scattering” (SAXS) in situ measurements. The SAXS data were correlated with ex situ data collected using TEM, XRD and uv-vis spectroscopy techniques. Using an Monte Carlo modeling method, the temporal evolution of the volume fractions and sizes of the nanoparticles were determined from the SAXS experimental data. An hypothesis for the growth mechanism based in Ostwald ripening and dynamic coalescence was discussed. The obtained results revealed that the nanoparticle system consists of two main populations.

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SURFACTANT-ASSISTED SYNTHESIS OF MO–V MIXED OXIDE CATALYSTS FOR UPGRADED ONE-STEP CONVERSION OF GLYCEROL TO ACRYLIC ACID

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The catalytic properties of Mo-V mixed oxides hydrothermally synthesized in the presence of ionic surfactants (SDS and CTAB) were investigated in the gas-phase oxidative dehydration of glycerol. The presence of surfactants promoted a change in morphology of the MoV2O8 phase, directing to the formation of rod-shaped crystals, and, consequently, an increase in macroporosity of materials, generated by intercrystallite spaces, when compared to a reference sample. Rod-like morphology stabilized the MoV2O8 mixed oxide phase during glycerol conversion, avoiding migration of vanadium from crystalline to amorphous phase, like observed in the reference sample, favoring the dynamic of reduction/reoxidation of vanadium and, consequently contributing to an increase in efficiency and stability of the catalyst. Both SDS-Mo-V and CTAB-Mo-V catalysts presented higher productivity of acrylic acid and good catalytic stability, with no coke formation and a considerable decrease in CO and CO2 evolution during 6 h of reaction. SDS-Mo-V presented the best catalytic results with 100% conversion, 57% of acrylic acid selectivity and 36% of COx selectivity. This study shows that due to the potential of these catalysts, it is important to forward into the establishment of the structure-activity relationship of these new catalysts with the modifications in their structural and textural properties (porosity and surface area) induced by organic structure-directing agents (SDS and CTA).

THE ROLE OF AMYLOGENIC FIBERS AGGREGATION ON THE ELASTICITY OF LIPID MEMBRANE

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This work presents a systematic study of the swelling behavior of a lecithin-lamellar phase to which the short sequence diphenylalanine (FF) is incorporated in different amounts. Small and wide-angle X-ray scattering configurations provide relevant information about the structure and elasticity of the lamellar stacking. These data show that important changes occur at the interface of the lipid membrane dependent, not only on the peptide content but also on the hydration of the lamellar structure. For instance, the multilamellar-unilamellar transition, previously observed for an increasing number of peptides, is now observed dependent on the hydration of the lamellar phase. Wide-angle X-ray scattering and electronic microscopy observations (TEM) provide experimental evidence of peptide aggregation into long fibers. We argue that the aggregates partition in water and may become large enough to destabilize the lamellar structure. It is also shown that, for a given peptide concentration, the lamellar structure can be rendered more flexible or more rigid, by tuning the hydration.

THE ROLE OF HYDRATION IN LIPID LAMELLAR PHASES CONTAINING SHORT PEPTIDE SEQUENCES : A SAXS STUDY

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Short peptide sequences containing phenylalanine are able to promote changes in several structural properties of lecithin membranes, which are dependent on the peptide/lipid (P/L) molar ratio. Particularly, the trimmer L-cysteine-L,L-diphenylalanine (CFF) was the most prominent interacting peptide, probably due to cysteine residues, which play a major role for membrane disruption in antimicrobial peptides (AMP) [1]. In this work, our attention was devoted to the study of hydration effect, known to also induce significant modifications in the lamellar properties [2]. The investigated complexes are composed by CFF and lecithin membranes. We used P/L between 0.001 and 0.1, and the small-angle x-ray scattering data was analyzed by a suitable model based on previous propositions [3]. From this investigation we were able to quantitatively investigate the role of hydration on the structure of the complex. It will be shown that, for both P/L, significant changes in structural parameters were observed along to a multi-unilamellar transition for P/L = 0.1, due to hydration increase, suggesting an important interplay between hydration and amount of peptide in the system. This work is supported by FAPESP (project number 2018/05888-3 and 2019/12301-1).

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WATER CONTENT EFFECTS ON THE POROSITY IN SITU DEVELOPMENT OF METAKAOLIN-BASED GEOPOLYMERS

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Cement systems should be designed to the life of the well. That implies they must work as a permanent solid barrier preventing fluid flow between different geological formations and to the surface. Therefore, a proper understanding of the mechanical properties, porosity and permeability are desirable. Geopolymers are ceramics obtained by the alkali activation of an aluminosilicate source that can replace Portland cement in oil well cementing operations. They are composed of a dense and predominantly amorphous matrix with a homogeneous footprint at macro and lower scales [1]. However, from sub-micro to nano-scales, the geopolymer morphology and nanostructure are a challenge to characterize, due to their intrinsic porosity and small agglomerated matrix particles [2]. Intrusive and small-angle scattering (SAS) techniques have been used to characterize the microstructure of bulk metakaolin based geopolymers [3]. The Vicat needle (VN), isothermal calorimetry (IC) and transit time (TT) of an ultrasonic pulse are methods commonly used to monitor and to elucidate the setting time, the kinetics, and the compressive strength evolution in Portland-based cement slurries [4; 5]. Within this context, this study presents the water content effects on the porosity in situ development of metakaolin-based geopolymers during the first 8 hours of the geopolymerization reaction. Additionally, a comparison between the techniques described before are made, in order to outline a correlation between the transition from liquid to solid state and the porosity evolution of Potassium metakaolin-based geopolymers, synthetized at room temperature, with increasing water content and designed to oil well applications purposes. BET, BJH and DFT models were applied to N2 adsorption data to obtain the total surface area and to estimate the pore size distribution. SAXS data are used to obtain the average pore sizes (using the SAS package and the Beaucage model), and the pore distributions calculated with the GNOM package, adopting a spherical pores model impregnated in a homogeneous matrix. VN, IC and TT data were used to determine the geopolymer hardening process, including its setting times. SAS techniques indicate an increase in surface area, average pore diameter and coarser pore distributions, over time, as the water content increases from the denser to the highest water content sample. VN and TT exhibit longer setting times; IC, slower kinetics development and, TT, a decrease in compressive strength evolution, as the water content increases from the denser to the highest water content sample. Differences in the quantitative results, based on the respective model assumptions, technical limitations and uncertainties in the true setting time and pore structure are presented, and microstructures are illustrated using SEM images.

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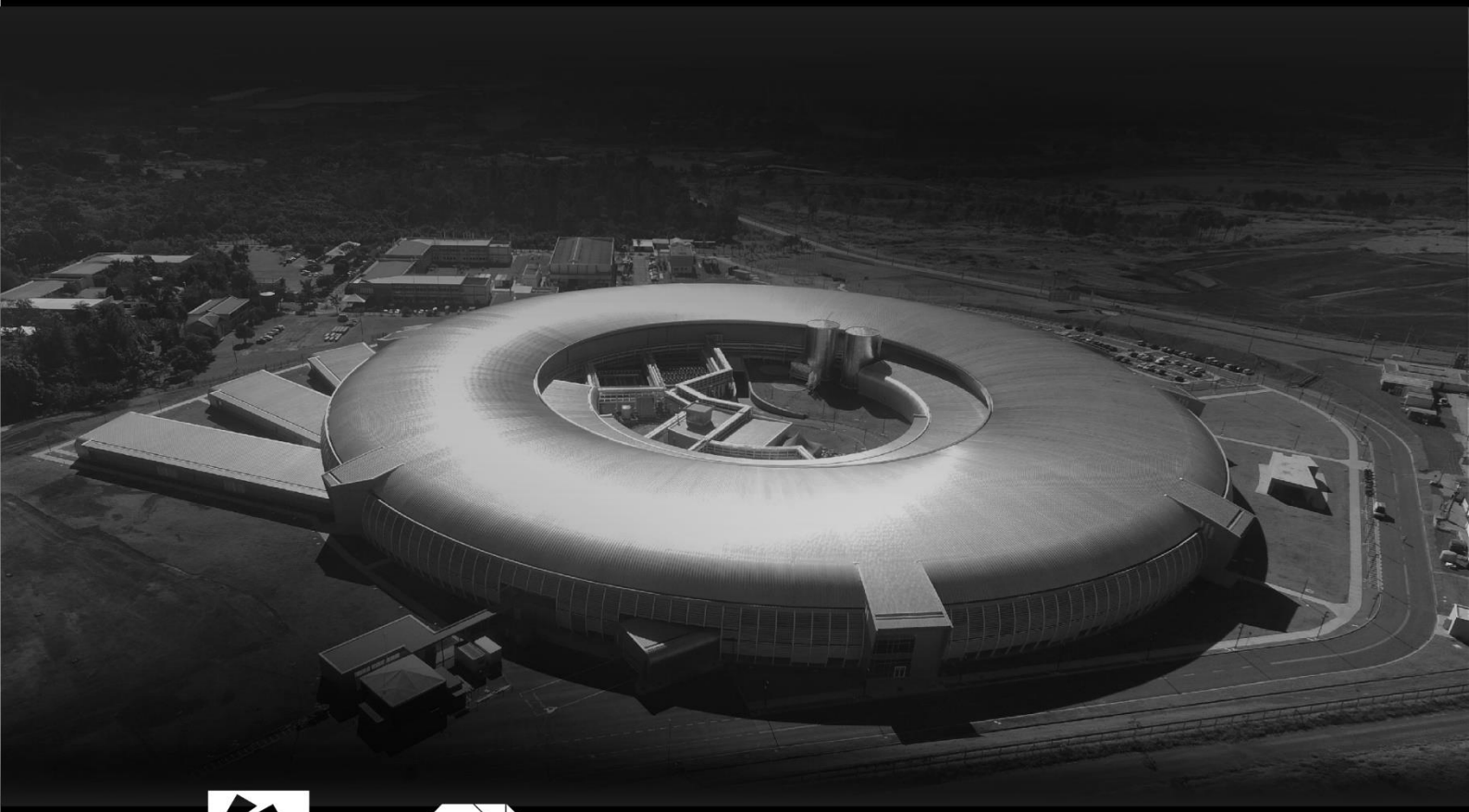

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